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INVESTIGATION OF SELECTED POTENTIAL ENVIRONMENTAL CONTAMINANTS: ASPHALT AND COAL TAR PITCH

FINAL REPORT

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16. ABSTRACT

This report reviews the literature on the potential environmental hazards and health impacts from production, distribution, and use of asphalt, the essentially uncracked residue from crude oil, and coal tar pitch, the highly cracked residue from fractional distillation of coal tar derived from the coking of coal. Topics include physical and chemical properties; production figures; uses; process descriptions; contamination potential; methods of sampling, monitoring, and analysis; acute and chronic effects on human health; toxicity to animals and plants; suggested handling practices; regulations and standards.

Of the 31 million tons of asphalt sold annually in the US, most is used in exposed surfaces: paving (78%), roofing (17%), dam linings and soil stabilizers, etc. (<5%). In contrast, 62% of the 1.2 million tons of pitch produced annually in the US is used in baked carbon and graphite products, 17% as fuel, and only 7% in exposed surfaces. Asphalt and pitch and their emissions and degradation products may contain varying quantities of trace metals and polycyclic aromatic hydrocarbons (PAH), some of which may have toxic effects including phototoxicity and cancer of skin and lungs. Potential environmental contamination and health hazards of asphalt and pitch are considered, with recommendations for further research.

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EXECUTIVE SUMMARY

Asphalt and coal tar pitch are bituminous materials used as binders, saturants and weatherproof coatings. Although they are similar in certain physical properties, they differ markedly in origin, composition, major uses, and severity of biological effects.

Asphalt

Petroleum asphalt is the residue, essentially uncracked, from the fractional distillation of crude oil. Small amounts of naturally occurring asphaltic materials are also used.

Commercial grades of asphalt are prepared to meet standard specifications based on physical properties. Base stocks of asphalt can be formulated from residues of distillation, solvent deasphalting, or air blowing processes. Liquid (cutback) asphalts are prepared by diluting base stocks with organic solvents. Emulsions of asphalt and water are also used.

Since 1970 annual asphalt sales in the United States have averaged 31 million tons. Seventy-eight percent of the asphalt is used in paving, 17% in roofing, and 5% in miscellaneous applications, including dam linings, soil stabilizers and electrical insulation.

Emissions from airblowing and from manufacture of paving and roofing materials have not been well characterized, but may contain entrained asphalt droplets, gases, trace metals, hydrocarbons, and large quantities of particulates which may contain polynuclear aromatic hydrocarbons (PAH), several of which are carcinogens.

A ninety-nine percent control level of the emissions from asphalt production and processing is possible using currently available thermal afterburners (fume incinerators) in conjunction with wet scrubbing units. Installation of paving and roofing materials may be a localized source of air pollution. Emissions can be greatly reduced by maintaining the asphalt heating kettle temperature below 216°C during roofing operations, and by using emulsions to replace cutback asphalts for paving.

Vast surfaces of asphalt covered roads, parking lots, runways and playgrounds are subject to microbial, chemical and physical degradation, which may produce some polycyclic aromatic, heterocyclic, and metallic substances, possibly toxic or carcinogenic, in air, waterways and sediments.

Limited animal skin painting and inhalation studies suggest that asphalt may be, at most, weakly carcinogenic. Other health hazards have not been demonstrated.

Few human exposure studies are available. Harmful effects from asphalt cannot be identified in exposures to mixtures of asphalt and the more biologically potent coal tar pitch, which have been common in paving, roofing, and weatherproofing operations. It is generally agreed that asphalt is a relatively harmless material to workers under proper working conditions (U.S. National Institute for Occupational Safety and Health, 1977a).

Present regulations limit particulate emissions from new asphalt hot mix plants and regulate effluent levels for new and existing paving and roofing point sources using tars and asphalts. The NIOSH recommended standard for occupational exposure to asphalt fumes is 5 mg airborne particulates per cubic meter of air (U.S. National Institute for Occupational Safety and Health, 1977a). Although the OSHA standard on "coal tar pitch volatiles" has been interpreted to include asphalt, the standard has not been successfully enforced.

Coal Tar Pitch

Crude coal tar is a highly cracked product evolved during carbonization of coal. All coal tar pitch commercially available in the U.S. is the distillation residue of by-product coke oven tar. The amount of pitch produced has declined from 2,004,000 tons in 1965 to 1,227,000 tons in 1976. About 62% of this pitch is used as a binder or impregnant in carbon and graphite products. The largest single carbon product market is for carbon anodes used in primary aluminum manufacture. About 17% of the pitch produced is burned as an open-hearth furnace fuel, and 7% is used for the manufacture of "tar" saturated roofing felt and for certain commercial roofs. A stable market for pitch (10,000 tons annually) has been its use as a binder in "clay pigeons" for skeet shooting. Pitch bonded and pitch impregnated refractory bricks used to line basic oxygen furnaces, blast furnaces and foundry cupolas represent a steadily growing market.

Pitch can undergo the same basic processing as does asphalt, namely air blowing, dilution with coal tar solvents, or emulsification with water. Emissions from manufacturing processes using pitch may include large amounts of pitch dust as well as pitch volatiles. Air pollution control measures used for asphalt fumes can also be used to contain emmissions from pitch. Large amounts of volatiles are emitted during the production of prebaked and graphitized pitch-containing carbon products, a major use of pitch. During use of such materials, higher levels of emissions are generated by self-burning electrodes than by those that have been prebaked or graphitized before use.

A large proportion of workers exposed to pitch and sunlight develop moderate to severe acute phototoxic reactions of the skin and eyes. Exposure to pitch and coal tar can cause skin cancer (U.S. National Institute for Occupational Safety and Health, 1977b). Inhalation of fumes and particulates may be related to increased incidence of lung cancer. Some cases of cancer of the bladder and certain other organs may be related to exposure to coal tar pitch. Although they do contain carcinogenic PAH, topical medications based on crude coal tar, which have been widely used for the prolonged treatment of chronic skin diseases, do not appear to have caused cancer in humans when properly used.

Some attempt has been made to control worker exposure to emissions from coal tar pitch. The present standard for "coal tar pitch volatiles" (other than coke oven emissions) specifies that worker exposure to airborne concentrations of pitch volatiles (benzene soluble fraction) shall not exceed 0.2 mg per cubic meter of air (U.S. Department of Labor, 1977). The current interpretation of the coal tar pitch volatile standard covers volatiles from distillation residues not only of coal, but also of other organic materials including petroleum (i.e., asphalt). Because coal tar pitch volatiles are considered carcinogenic, the National Institute for Occupational Safety and Health (1977b) has recommended a standard for occupational exposure to coal tar products, including coal tar pitch, of 0.1 mg cyclohexane solubles per cubic meter of air (the lowest detectable limit).

Examination of the literature indicates that the biological effects of asphalt are probably limited. Large quantities, however, are processed and the major uses are in roofing and paving products that are permanently exposed to slow degradation in the environment. Coal tar pitch, on the other hand, produces acute effects in a large proportion of exposed workers as well as possible increased risk of cancer of several sites after prolonged exposure. The major uses of pitch involve occupational rather than environmental exposure.

INTRODUCTION

Asphalt and coal tar pitch are used in a variety of industrial processes and manufactured products that utilize their properties as thermoplastic, durable, cementitious, water-resistant materials. The Environmental Protection Agency, Office of Toxic Substances, has requested a preliminary literature investigation of the environmental contamination potential of these two bituminous materials. This noncritical review is intended to serve as a source of information to be used in evaluation of the severity of the environmental hazard and the need for further action concerning these two materials.

In this report, "asphalt" is considered to be the residue, essentially uncracked, from the fractional distillation of crude petroleum. Coal tar pitch is defined as the residual product from the distillation of crude coal tar, a cracked material, which is formed during the coking of coal.

A survey of the literature since 1954 was conducted, referring to older literature when recent information was unavailable. The literature review includes composition and properties; production figures and process descriptions; contamination potential from manufacture and use; analysis; toxicity and carcinogenicity to humans, animals, and plants; recommended handling practices; legislation; and standards. Conclusions and recommendations based on the literature are also presented.

GLOSSARY

ASPHALT - A black to dark-brown solid or semisolid cementitious material in which the major constituents are bitumens. Asphalt occurs naturally (asphaltites and native asphalts) or is obtained as the residue, essentially uncracked, from the straight distillation of petroleum.

BITUMEN - A mixture, completely soluble in carbon disulfide, of hydrocarbons of natural and/or pyrogenous origin and their nonmetallic derivatives.

BITUMINOUS MATERIAL - A mixture, containing bitumen or constituting the source of bitumen, occurring as natural (asphaltite, tar sand, oil shale, petroleum) or manufactured (coal tar pitch, petroleum asphalt, wax) material.

COAL TAR - A brown or black bituminous material, liquid or semisolid in consistency, obtained as the condensate in the destructive distillation (coking) of coal, and yielding substantial quantities of coal tar pitch as a residue when distilled.

COAL TAR PITCH - A black or dark-brown material obtained as the residue in the partial or fractional distillation of crude coal tar. As contrasted to petroleum asphalt, which is essentially uncracked, coal tar pitch is a highly cracked material.

COAL TAR PITCH VOLATILES - The fumes from the distillation residue of coal tar. In legal use, this term refers to the volatiles from the distillation residues of coal, petroleum or other organic matter. In this report, use of this term in connection with asphalt fumes has been avoided except in discussion of the legal definitions.

CRACKING - A process (e.g., pyrolysis, thermal treating, coking) whereby large molecules (as in oil or coal) are decomposed into smaller, lower boiling molecules, while reactive molecules thus formed are recombined to create large molecules (including PAH) different from those in the original stock.

PETROLEUM PITCH - A cracked product resulting from pyrolysis of gas oil or fuel oil tars. Because it shares certain properties with coal tar pitch, it has been suggested as a replacement for it in some applications. This term should never be used to refer to an asphalt product. Petroleum pitch is not included within the scope of this report.

Abbreviations:

BaP	Benzo(a)pyrene
BeP	Benzo(e)pyrene
CTPV	"Coal tar pitch volatiles" (see Glossary)
PAH	Polynuclear aromatic hydrocarbons
PNA	Polynuclear aromatic compounds, including both hydrocarbons and heterocyclics (use in this report has been avoided)
PPOM	Particulate polycyclic organic matter

I. PHYSICAL AND CHEMICAL PROPERTIES

A. Bituminous Materials

Asphalt and coal tar pitch belong to a group known as bituminous materials. Bitumens are defined as mixtures of hydrocarbons and their nonmetallic derivatives of natural or manufactured origin, which are completely soluble in carbon disulfide (Hoiberg, 1965a,b).

In British and European usage, however, the term "bitumen" is used to refer to the material known in the United States as "asphalt." Among the many materials which may be considered as bituminous, only native and manufactured asphalts and manufactured coal tar pitch, as shown in Figure I-1, will be discussed in this review.

Asphalt is a dark brown to black cementitious solid or semisolid material, composed predominantly of high molecular weight hydrocarbons, occurring either as a native deposit or as a component of crude petroleum, from which it is separated as a distillation residue without pyrolysis. The asphalt content of crude oils varies from 9 to 75% (Ball, 1965), and the nature of the asphalt varies with its parent crude. About 98% of the asphalt used in the United States is derived from crude petroleum (Miles, 1977).

Coal tar pitch is the distillation residue of crude coal tar, which is a pyrolysis product from the high temperature carbonization (coking) of coal. Coal tar pitches, brownish black to black in color and containing at least 5000 compounds, range from viscous liquids at ordinary temperature to materials which behave as brittle solids exhibiting a characteristic conchoidal fracture (McNeil, 1969).

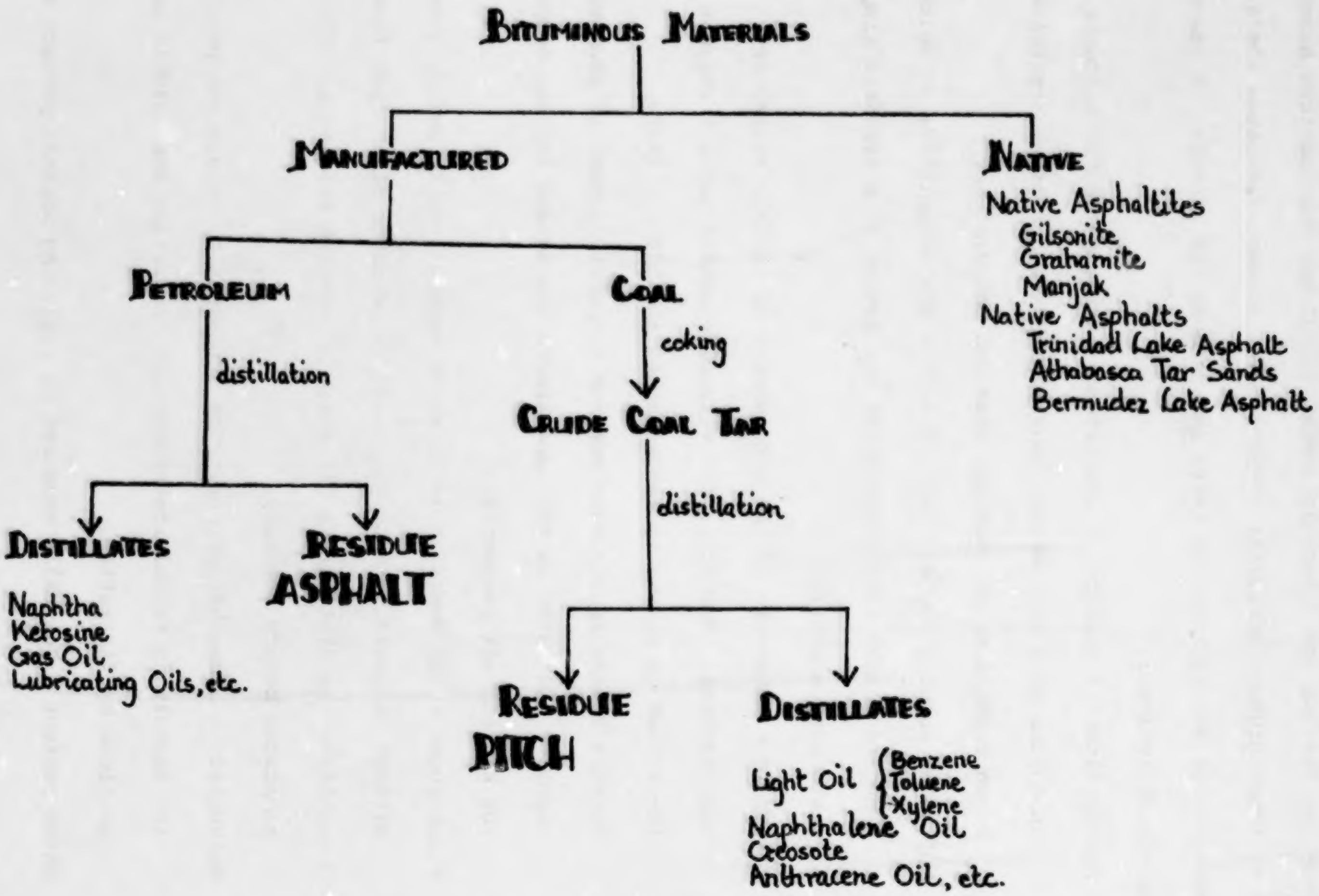

BITUMINOUS MATERIALS
MANUFACTURED
NATIVE
Native Asphaltites
Gilsonite
Grahamite
Manjak
Native Asphalts
Trinidad Lake Asphalt
Athabasca Tar Sands
Bermudez Lake Asphalt
PETROLEUM
distillation
DISTILLATES
Naphtha
Kerosine
Gas Oil
Lubricating Oils, etc.
RESIDUE
ASPHALT
COAL
coking
CRUDE COAL TAR
distillation
RESIDUE
PITCH
DISTILLATES
Light Oil
Benzene
Toluene
Xylene
Naphthalene Oil
Creosote
Anthracene Oil, etc.

FIGURE I-1. PARTIAL CLASSIFICATION OF BITUMINOUS MATERIALS

Because the uses of asphalt and pitch depend largely on physical properties, specifications are based on empirical tests using strictly defined procedures. Most of these tests are covered by standards of the American Society for Testing and Materials (ASTM) (1973) and the American Association of State Highway Officials (AASHO). The Asphalt Institute (1974a) presents brief descriptions of tests and methods for asphalt. A few of these tests are as follows:

Penetration - a measure of consistency expressed as the distance, in tenths of a millimeter, that a standard needle penetrates under known conditions of loading, time and temperature.

Softening point (ring and ball, R & B) - the temperature at which a standard weight ball sinks below the bottom of a standard ring containing asphalt.

Viscosity - a measure of the consistency of asphalt at two set temperatures. Normally, the viscosity-graded asphalt cements are identified by viscosity ranges at 60 and 135°C. Sixty degrees is the approximate maximum temperature used in pouring asphalt, and 135°C is the approximate mixing and laydown temperature for hot asphalt pavements.

Flash point - the temperature to which asphalt may be safely heated without an instantaneous flash in the presence of an open flame.

Ductility - the distance in air which a standard briquet at 25°C can be elongated before breaking.

Solubility - a measure of purity of the asphalt, determined by dissolving the asphalt in trichloroethylene and separating the soluble and insoluble portions by filtration.

Water content - generally measured by refluxing asphalt product with xylol or high-boiling-range petroleum naphtha and collecting and measuring the water condensate in a trap.

Specific gravity - the ratio of the weight of a given volume of bituminous material to that of an equal volume of water at the same temperature, usually reported as 77/77°F.

B. Asphaltic Materials

1. Petroleum Asphalt

a. Composition of crude oil

As indicated in the beginning of this chapter, the asphalt content of crude oil varies (9-75%) and the nature of asphalt varies with its parent crude. Crude oil is a very complex mixture and no single crude oil has ever been completely defined (Rossini and Mair, 1951, 1959; Rossini *et al.*, 1953; Altgelt and Gouw, 1975). The enormous diversity of different crude oils extends from light oils to heavy types found in asphalt lakes. These variations are found not only in the viscosity, but also in the content and length of paraffinic chains, number of aromatic carbon atoms, degree of ring fusion and type and amount of hetero atoms.

More than several hundred compounds have been identified in Ponca City (Oklahoma) crude oil. They have been classified into nonpolar and polar materials. The nonpolar group includes straight chain alkanes, (hexane, pentane), branched alkanes (isooctane), cycloalkanes (butylcyclohexane), and aromatics (propylbenzene and propyltetralin). The polar group includes acids such as naphthenic acids, phenols, alkylthiols, cycloalkylthiols, alkylthiophenes, pyridines, quinolines, indoles, pyrroles and porphyrins. Nickel (49-345 ppm, Berry and Wallace, 1974) and vanadium (0.3 to 0.6 weight percent) are the most prominent trace metals that occur in petroleum (Atlas and Bartha, 1973; Yen, 1972). Calcium, magnesium, titanium, cobalt, tin, zinc, and iron are also metals commonly found in crude petroleum. These metals tend to accumulate in the residue.

b. Types of petroleum asphalts

Distillation is the primary means for separating crude petroleum fractions. Asphalt is the high-boiling residual fraction. Crude oil may be distilled first at atmospheric pressure to remove the lower boiling fractions such as gasoline or kerosine and then can be further processed by vacuum distillation, leaving a straight-run asphalt. The asphaltic residue may also be processed with liquid propane or butane. Vacuum distillation and propane deasphalting both affect the hardness of the residue. When processed from the same stock, propane deasphalted residue differs little from straight-run residue (Corbett, 1966; Hoiberg et al., 1963; Hoiberg, 1965a). Straight-run asphalt accounts for 70 to 75% of all the asphalt produced.

Airblown asphalts with modified properties as compared to straight run asphalt are produced from the asphalt stock by treatment with air at temperatures of 200 to 280°C. Catalysts such as phosphorus pentoxide, ferric oxide or zinc chloride, used in concentrations from 0.1 to 3%, reduce the air blowing time. The asphalt undergoes dehydrogenation and polymerization by ester formation and carbon linkage (Smith and Schweyer, 1967; Haley, 1975; Corbett, 1975) during these processes. The presence of dicarboxylic anhydrides in oxidized asphalts has been confirmed by infrared spectroscopy (Petersen et al., 1975). There is a decrease in the aromatic resin content and an increase in the asphaltene content and hydrogen bonding basicity of airblown asphalt (Barbour and Petersen, 1974). Air blowing results in a product with a higher softening point for given penetration than straight reduced asphalt, while catalytic air blowing produces a still higher softening point. Air blown asphalt, which accounts for 25 to 30% of asphalts used, is a viscous material that is less susceptible to temperature change than straight run asphalt.

Treatment of asphalt at high temperature (480-590°C) and pressure (200 psig) produces thermal asphalts, less than 5% of total production of asphalt, which are not commonly available because catalytic cracking for the production of gasoline has largely replaced thermal cracking. Such asphalts are characterized by a relatively high specific gravity, low viscosity and poor temperature susceptibility (little change in consistency with increased temperature). They have a lower hydrocarbon to carbon ratio than straight run asphalts. Highly cracked residues have infrared spectra similar to those of coal tar pitches (Corbett, 1965; Hoiberg et al., 1963; Hoiberg, 1965a). The viscosity is more susceptible to temperature change in thermal asphalts than in straight run asphalt.

An elemental analysis of asphaltic residues (% by weight) shows carbon ranging from 80 to 89%, hydrogen from 7 to 12%, oxygen from 0 to 3%, sulfur from trace to 8% and nitrogen from trace to 1% (Table 1-1).

c. Fractionation of asphalt

The high molecular weight (M.W. 100-2500) asphaltene fraction is precipitable by n-pentane, hexane or naphtha and, despite source, appears constant in composition as determined by carbon-hydrogen analysis. Asphaltenes are solid at room temperature and show some degree of crystallinity by X-ray diffraction. The concentration of asphaltenes to a large extent determines the viscosity of asphalt (Altgelt and Harle, 1975; Reerink, 1973; Reerink and Lijzenga, 1973).

Maltenes, the nonprecipitated fraction, are generally considered to contain resins (M.W. 500-1000) characterized by high temperature susceptibility that are either adsorbed on activated clays or precipitated by sulfuric acid

TABLE I-1. ELEMENTAL ANALYSES OF ASPHALT FRACTIONS AND NATURAL ASPHALTS

	Softening point (ring and ball) °C	Penetration, 20.5°C	Elemental analyses, % by wt					Atomic ratio, C/H
			C	H	S	N	O[a]	
Petroleum								
Straight run	50-70	12-46						
asphaltenes			80.5-83.5	7.3-8.0	4.6-8.3	0.4-0.9	0-1.8	0.85-0.97
petrolenes			82.0-84.8	10.0-10.6	0.4-5.5	0.5-0.5	0.7-1.4	0.65-0.70
Air-blown	80-90	21-38						
asphaltenes			80.7-84.8	7.8-8.2	3.7-7.3	0.5-0.8	2.0-2.8	0.82-0.88
petrolenes			82.5-84.3	10.9-11.5	2.3-5.4	0.4	0.8-1.3	0.62-0.64
Highly cracked	50	36						
asphaltenes			88.9	5.9	3.0	0.4		1.25
petrolenes			87.9	7.9	3.7	0.5		0.93
Native								
Trinidad	90-91	1.5-4	80.82	10.7	6.8	0.8		0.64
Bermudez	60-70	20-30	82.9	10.8	5.9	0.8		0.64

[a] Oxygen determined by difference

Sources: Hoiberg et al., 1963

or a solvent (acetone, isobutyl alcohol, propane). The nonprecipitable maltene fraction consists of oils (M.W. 250-600) which may contain appreciable quantities of wax and are characterized by low temperature susceptibility.

The petrolene fraction (M.W. 500-1000) boils below 300°C and is soluble in low-boiling saturated hydrocarbons such as n-pentane.

In addition, asphalts may contain saponifiable material and acids, the content of which is determined as percent naphthenic acids in the original crude (Corbett, 1966; Hoiberg, 1965a; Hoiberg et al., 1963).

Most separations of asphalt into its constitutional components rely on some type of preliminary fractionation (Figure 1-2) prior to the use of gel permeation, gas-liquid, paper, gravity fed column or high performance chromatography (Couper, 1977; Schweyer, 1975). The fractions obtained are then further analyzed by use of ultraviolet spectrometry, nuclear magnetic resonance, infrared spectroscopy, electron spin resonance, atomic absorption or X-ray diffraction, as described in Chapter IV.

Five principal operations (distillation, extraction, adsorption, precipitation and chromatography) are used in various combinations for the fractionation of asphaltic bitumens (Rostler, 1965; Hoiberg, 1965a; Hoiberg et al., 1963) to produce a variety of fractions that can be classified into a few general groupings (Figure I-2). However, none of these fractionation methods have provided satisfactory results when used separately.

Distillation

Distillation is used to concentrate the asphaltenes and maltenes and to separate out the petrolenes. However, this method by itself is not useful as an analytical separation procedure for complex mixtures (Hoiberg,1965).

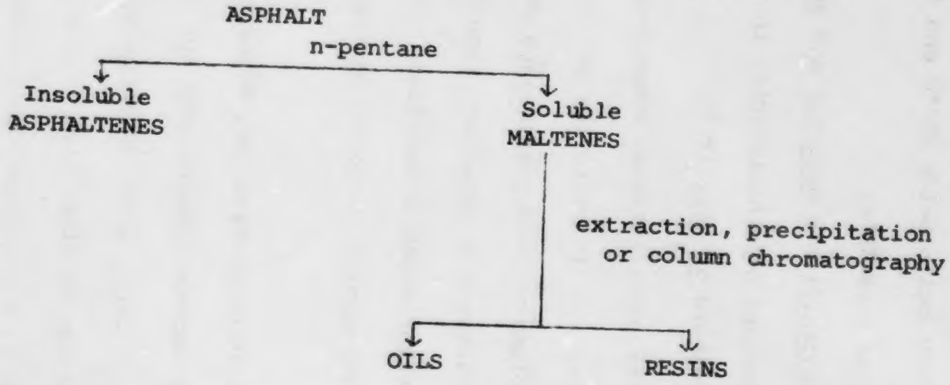

ASPHALT
n-pentane
Insoluble
ASPHALTENES
Soluble
MALTENES
extraction, precipitation
or column chromatography
OILS
RESINS

FIGURE I-2. FRACTIONATION OF ASPHALT

Extraction

Carbon disulfide has been used in the separation of asphalt into low boiling petrolenes and a residual fraction, while n-pentane has been used as a means of fractionating asphalt into asphaltenes and maltenes. However, these types of extractions give only a partial separation of asphalts (Rostler, 1965).

A more complex separation involves the Hoiberg method (Hoiberg and Garris, 1944) which separates the asphalt stepwise into five fractions: (1) asphaltenes (2) hard resins, (3) waxes, (4) soft resins, and (5) oils. The Traxler-Schweyer method (1953), a simplified Hoiberg method, consists of stepwise separation into (1) asphaltenes precipitated by n-butanol and (2) a n-butanol-soluble fraction consisting of paraffins and naphthenes. Lastly, the method of Knowles *et al.* (1958) involves stepwise fractionation into (1) asphaltenes, (2) soft and hard resins, (3) waxes and (4) paraffinic and naphthenic oils. This last method is valuable because it separates asphalts into waxes, two types of resins and two kinds of oils.

Adsorption

Fractionation by adsorption has involved charcoal, charcoal and sand, and various kinds of molecular sieves. Early methods consisted of heating mixtures of liquid bitumens with adsorbents such as charcoal and fuller's earth, followed by filtration. They are considered the predecessors of modern chromatographic methods, which use the principles of both solvent extraction and adsorption. Molecular sieves can still be considered to be a relatively new tool which is being incorporated into separation procedures for asphaltic bitumens (Rostler, 1965; Couper, 1977).

Chromatography

A number of fractionation methods have used chromatography, either by itself or in combination with extraction and adsorption methods. Silica gel is used to separate maltenes into resins and oils and maltenes or asphaltenes into non-aromatics, aromatics and polar compounds. The Glasgow-Termine method, which also uses silica gel, elutes two pentane fractions and one fraction each of benzene, carbon tetrachloride and ethanol, while the Hubbard-Stanfield method involves (1) precipitation of asphaltenes with n-pentane, (2) elution of oils from alumina with n-pentane and (3) elution of resins from alumina with methanol-benzene mixture. In each of these methods, however, the overlapping of components from each fraction is typical for these chromatographic techniques (Rostler, 1965).

Two elaborate methods have been attempted by Kleinschmidt (1955) and O'Donnell (1951). The Kleinschmidt method involves (1) precipitation of asphaltenes with n-pentane, (2) elution of the n-pentane soluble fraction from fuller's earth to obtain (a) white oils with n-pentane, (b) dark oils with methylene chloride, (c) asphaltic resins with methyl ethyl ketone, and (d) a black residue desorbed with a mixture of acetone and chloroform. The O'Donnell method involves molecular distillation on the basis of molecular size followed by silica gel chromatography to separate saturates, aromatics, and resins. The saturates are dewaxed followed by urea-complex formation to separate long chain paraffins, and the aromatics are separated by alumina chromatography into mono- and di-cyclic aromatics, followed by peroxide oxidation and another chromatography to separate the benzothiophene analogs.

Precipitation

The chemical precipitation methods use excess amounts of reagents to remove one component or fraction from the complex mixture. One method (Rostler, 1965) involves the precipitation of asphaltenes by low boiling hydrocarbons, followed by precipitation with sulfuric acid. The Rostler-Sternberg method (1949) involves precipitation of asphaltenes with n-pentane and selective precipitation of the nitrogen bases and acidaffins 1 and 2 by use of successive concentrations of H_2SO_4 (85%, 98%, fuming (SO_3)). The applicability of these methods to complex mixtures is still under investigation. A more recent method by Corbett (1969) uses n-heptane, benzene, and methanol-benzene-trichloroethylene as solvents to obtain petrolenes, asphaltenes, saturates, aromatics and polar fractions.

All of the methods and combinations described above, as well as others described in reviews (Couper, 1977; Schweyer, 1975; Altgelt and Harle, 1975), have been used in analysis of the complex mixtures of various types of asphalts. Figure I-3 shows a composite stepwise fractionation of the various components of asphalt.

Techniques such as solvent fractionation, thermal diffusion and sulfuric acid precipitation and chromatography have yielded asphaltic fractions that have been examined using infrared (Petersen et al., 1971) and ultraviolet spectrometry, X-ray diffraction, nuclear magnetic resonance, electron spin resonance and atomic absorption (Couper, 1977).

Little is known at present about polynuclear aromatic hydrocarbons (PAH) in asphalt. Wallcave et al. (1971) have presented average concentrations of PAH in asphalt obtained from various sources (Table I-2). More work needs to be done in the area of PAH determinations in asphalt.

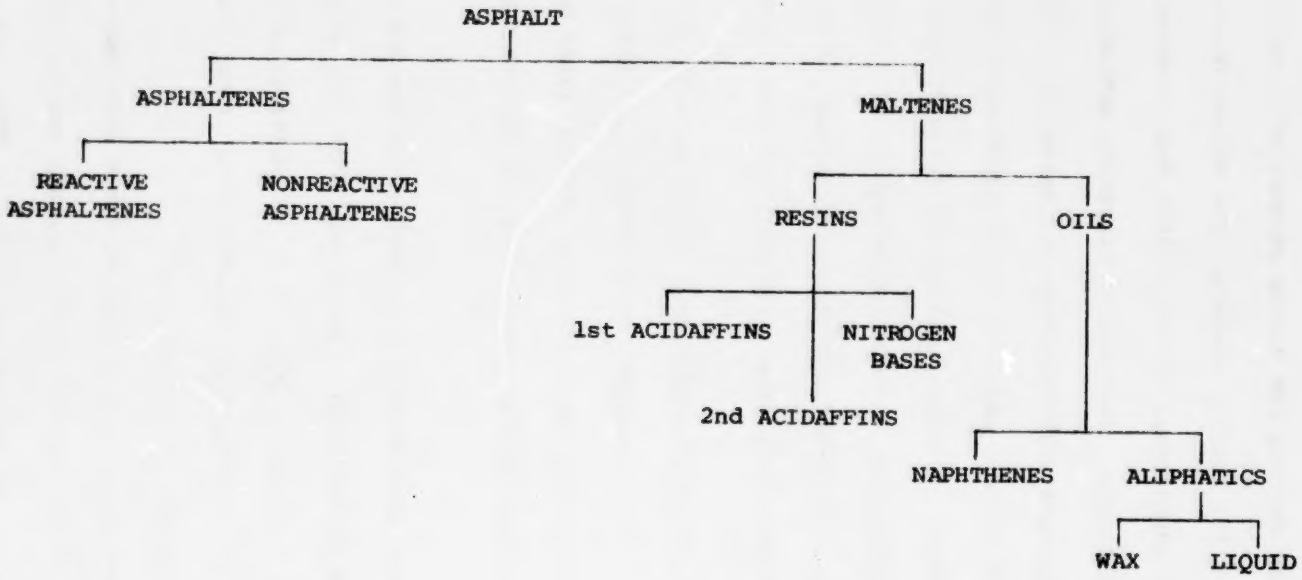

ASPHALT
ASPHALTENES
MALTENES
REACTIVE ASPHALTENES
NONREACTIVE ASPHALTENES
RESINS
OILS
1st ACIDAFFINS
NITROGEN BASES
2nd ACIDAFFINS
NAPHTHENES
ALIPHATICS
WAX
LIQUID

FIGURE I-3. STEPWISE FRACTIONATION OF VARIOUS COMPONENTS OF ASPHALT

TABLE I-2. CONCENTRATION AVERAGES OF SEVERAL PARENT PAH IN ASPHALT (ppm)

Asphalt	Phenanthrene	Pyrene	Benz[a]-anthracene	Tri-phenylene	Chrysene	Benzo[a]-pyrene	Benzo[e]-pyrene	Perylene	Benzo[ghi]-perylene	Coronene
1	2.3	0.6	0.15	0.25	0.2	0.5	3.8	-	2.1	1.9
2	0.4	1.8	2.1	6.1	8.9	1.7	13	39	4.6	0.8
3	3.5	4.0	1.1	3.1	2.3	1.3	2.9	2.2	1.0	0.5
4	1.3	8.3	0.7	3.4	3.9	2.5	3.2	6.1	1.7	0.2
5	0.6	0.9	0.9	3.8	3.2	1.6	6.5	2.9	2.7	0.9
6	∼35	38	35	7.6	34	27	52	3.0	15	2.8
7	1.1	0.3	0.2	1.0	0.7	0.1	1.6	0.1	0.6	0.9
8	∼2.3	0.08	-	0.3	0.04	-	0.03	-	Trace	-

Benzofluorenes, fluoranthene, benzo[k]fluoranthene, anthracene, picene and indeno[1,2,3-cd]pyrene are present in trace amounts.

Source: Wallcave et al., 1971

As indicated previously, some of the metals present in crude oil tend to accumulate in the asphalt. Vanadium, nickel, and iron tend to be concentrated in the asphaltene fraction (Corbett, 1967). Vanadium chelates have been studied in petroleum asphaltenes (Tynan and Yen, 1969; Wolsky and Chapman, (1960).

Other metals are bound to polynuclear aromatic compounds containing sulfur, nitrogen and oxygen polar groups as well as naphthenic and paraffinic side chains. During air blowing, these polynuclear aromatics are converted to asphaltenes. Removing the asphaltene fraction from blown asphalt can remove up to 97% of the organometallics.

2. Native Bitumens

Native bitumens include a wide variety of natural deposits ranging in character from crude oil to sand and limestone strata impregnated with bituminous material. Only a few of these materials are classified as asphalts.

a. Native asphalts

The native asphalts include a variety of reddish brown to black materials of semisolid, viscous-to-brittle character. They can occur in relatively pure form, with 92 to 97% soluble in carbon disulfide and only 3 to 8% mineral content, as is the case for Bermudez (Venezuela) lake asphalt, or in less pure form, with a carbon disulfide-soluble fraction of 39% and a mineral content of 27%, as is the case for Trinidad lake asphalt (Table I-1). Trinidad lake asphalt is dull black and semiconchoidal in fracture, with a penetration of 10 at 30°C and a softening point (R & B) of 85°C. When gas and water are driven off at 100°C, Trinidad asphalt loses 29% of its weight and the carbon disulfide-soluble fraction increases to 56% while the mineral content increases to 38%.

Frequently, the bitumen is found in pores and crevices of sandstones, limestones or argillaceous sediments and is known as rock asphalt. The term "tar sands" has been used by geologists to designate sands impregnated with dense, viscous asphalt found in certain sedimentary structures, such as the Athabasca tar sands now being mined in Alberta, Canada (Hanson, 1964; Broome, 1965; Camp, 1969; Breger, 1977).

b. Asphaltites

Asphaltites are naturally occurring, dark brown to black, solid, and relatively nonvolatile bituminous substances differentiated from native asphalts primarily by their high content of n-pentane insoluble material (asphaltene) and their high temperature of fusion, 115 to 330°C (R & B). Among these are gilsonite, grahamite and manjak, all of which are in the pure state, with close to 100% carbon disulfide solubility and less than 5% mineral content. Gilsonite, the native asphaltite most commonly used, is found in western Colorado and eastern Utah. It is black in color with a bright luster, a conchoidal fracture, and a penetration at 41°C of 3 to 8 with a softening point (R & B) of 230 to 350°F (110 to 177°C). Gilsonite has a carbon content of 85 to 86%, is soluble in carbon disulfide to 98%, and has a specific gravity of 1.03 to 1.10 at 25°C (77°F).

Grahamite is found in a single vertical fissure in a sandstone in West Virginia. It has a specific gravity of 1.15 to 1.20 at 77°F and a softening point (R & B) of 350 to 600°F (177 to 315°C), and a high temperature of fusion which distinguishes it from gilsonite. Other deposits in the United States, as well as in Mexico, Cuba and certain areas of South America, have yielded bitumens corresponding in general to the grahamite in West Virginia, and are therefore referred to under this name.

A third broad category is known as glance pitch or manjak, originally mined in Barbados, West Indies. The specific gravity at 77°F (25°C) is 1.10 to 1.15, with a carbon content of 80 to 85%, a softening point (R & B) of 230 to 350°F (110 to 177°C), a carbon disulfide soluble fraction of 95%, a black color and a bright to fairly bright luster with a conchoidal to hackly fracture. This asphaltite is considered an intermediate between grahamite and gilsonite because of its specific gravity and fixed carbon (Broome, 1965; Hanson, 1964; Hoiberg et al., 1963; Breger, 1977).

C. Coal Tar Pitch

1. Source

Coal can be described as a compact stratified mass of vegetation, interspersed with smaller amounts of inorganic matter, which has been modified chemically and physically by agents over time. These agents include the action of bacteria and fungi, oxidation, reduction, hydrolysis and condensation, and the effects of heat and pressure in the presence of water. The chemical properties of coal depend upon the amounts and ratios of different constituents present in the vegetation, as well as the nature and quantity of inorganic material and the changes which these constituents have undergone (Francis, 1961).

Coal, therefore, has a rather complicated chemical structure based on carbon and hydrogen with varying amounts of oxygen, nitrogen and sulfur. Bituminous coal, from which coal tar pitch is derived, contains a number of PAH, including carcinogenic benzo(a)pyrene (BaP) and benz(a)anthracene (Tye et al., 1966), and a variety of toxic trace elements such as antimony, arsenic, beryllium, cadmium, lead, nickel, chromium, cobalt, titanium, and vanadium (Zubovic, 1975).

When coal is pyrolyzed, a variety of changes occur: above 100°C free water evaporates; above 200°C combined water and carbon dioxide are evolved; above 350°C bituminous coals soften and melt, decomposition begins, and tar and gas are evolved; at 400 to 500°C most of the tar is evolved; at 450 to 550°C decomposition continues and the residue turns solid; above 550°C the solid becomes coke and only gas is evolved; around 900°C no more gas is evolved and only coke remains; above 900°C small physical changes occur

When coal undergoes carbonization, it passes through two steps of decomposition: onset of plasticity at 350 to 500°C and advanced decomposition at 650 to 750°C. Volatile products released at each stage undergo a series of secondary reactions as they pass through the coke before emerging from the retort. The volatiles are separated by fractional condensation or absorption into tar, ammoniacal liquor, benzole, and illuminating or heating gas (McNeil, 1966a).

The major reactions in the conversion of primary carbonization products into tars (McNeil, 1966a) are:

1) cracking of higher molecular weight paraffins to gaseous paraffins and olefins;

2) dehydrogenation of alkylcyclic derivatives to aromatic hydrocarbons and phenols;

3) dealkylation of aromatic, pyridine and phenol derivatives;

4) dehydroxylation of phenols;

5) synthesis of PAH by condensation of simpler structures;

6) disproportionation of PAH to both simpler and more complex structures.

The temperature of carbonization and contact time with the hot coke bed and heated walls of the retort will determine the composition of tars, as well as the extent of the reactions. Tars from the different types of carbonization processes vary widely as to their composition and characteristics.

The term low temperature carbonization refers to pyrolysis of coal to a final temperature of 700°C. The final solid product is a weak coke with high yields of tar and oil and low yield of gas. High temperature carbonization is pyrolysis of coal between 900°C and 1200°C, with town gas as the product and coke as the by-product at the lower temperature and metallurgical coke as the product and gas as the by-product at the higher temperature (Encyclopaedia Britannica, 1974).

Coal tar pitch is the residue from the processing of coal tar (Figure I-4). Pitches or "refined tars" are obtained from the distillation of tars and represent from 30 to 60% of the tar components (McNeil, 1966a) (Table I-3). Distillate oils (described later) obtained by steam or vacuum distillation of pitch or pitch crystalloids or from coking of pitch are the only fractions from which pure chemical compounds are isolated.

McNeil (1966a) has described the change in composition of tars found as the temperature increases from vacuum distillation or low temperature carbonization to high temperature carbonization:

(a) The amounts of paraffins and naphthenes decrease and disappear, the naphthenes fading out before the paraffins.

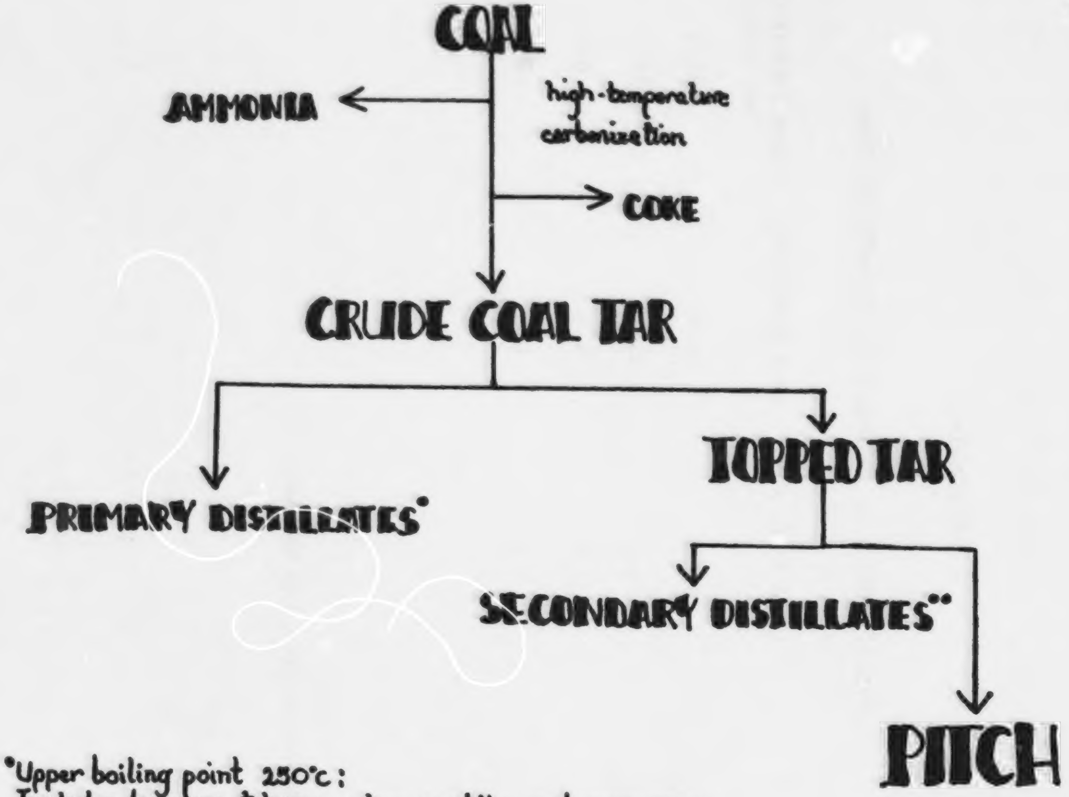
(b) The amount of phenolic material falls from about 30% to a small value.

(c) The proportion of aromatic hydrocarbons increases from a low figure to over 90%.

(d) The proportions of aromatic, phenolic and heterocyclic compounds containing alkyl side chains decrease markedly.

(e) The proportion of condensed ring compounds containing more than three fused rings increases.

(f) The yield of coal carbonized decreases from 10% to less than 5%.


COAL
AMMONIA
high-temperature carbonization
COKE
CRUDE COAL TAR
PRIMARY DISTILLATES*
TOPPED TAR
SECONDARY DISTILLATES**
PITCH

*Upper boiling point 250°C:
Includes benzene, toluene, xylene, naphtha and coumarone.
**Includes anthracene and creosote fractions.

FIGURE I-4. ORIGIN OF COAL TAR PITCH

TABLE I-3

TYPICAL ANALYSES (PERCENT BY WEIGHT) OF TARS

	Coke Oven Tar	Gas Works Tar	Low Temperature Tar (200°C)
Pitch	59.0	44.0	26.0
Creosote	31.0	42.0	55.0
Light Oils	2.5	5.4	6.7
Heavy Oils	5.4	6.5	9.4

Source: Encyclopaedia Britannica, 1974

2. Physical Properties

Coal tar pitch is a black or brownish black shiny material ranging from a viscous liquid at ordinary temperatures (30 to 80°C) to a material which behaves as a brittle solid exhibiting a characteristic conchoidal fracture (McNeil, 1966a; Lauer, 1974). At higher temperatures the brittle solid pitch can become a viscous liquid. It has a characteristic "tarry" odor described as a combination of smells of naphthalene and phenol modified by small amounts of pyridine and thiophenol.

The residue from the primary distillation can have different viscosity grades depending on how extensively the coal tar is distilled. If the distillation is continued to the desired softening point, the residue is called "straight run" pitch to distinguish it from "cut-back" or "flux-back" pitch, which is a straight run pitch of harder consistency cut back to the desired softening point with tar-distillate oil (McNeil, 1969).

Since pitch is composed of a great number of different compounds, it does not show a distinct melting or crystallizing point. Therefore, pitch is usually characterized by the softening point, which can be determined by one of several standard methods: ring and ball, cube in air, cube in water and Kramer-Sarnow (McNeil, 1966b). Each of these methods represents the temperature at which a given viscosity or softness is attained under specific conditions.

The softer grades of pitch having softening points (R & B) below 50°C are usually referred to as base tars or refined tars; other grades are soft pitch (50 to 75°C), medium-hard pitch (85 to 95°C), and hard pitch (above 95°C) (McNeil, 1969).

In general, all pitches behave essentially as Newtonian liquids over the range of viscosities which can be measured reliably. The only departure from Newtonian flow in pitches is a slight reduction in viscosity with increasing shearing stress found in samples with a high content of toluene insoluble materials.

3. Chemical Properties

It has been difficult to isolate and characterize compounds from this complex bituminous material. It has been estimated that pitch contains five to ten thousand compounds, of which 100 to 150 have been isolated and identified (McNeil, 1966b). Among those identified have been a large number of PAH. Varying amounts of PAH are formed by secondary reactions occurring during carbonization of coal.

Coal tar pitch is composed predominantly of carbon (86 to 93%) and hydrogen (5 to 7%), with small amounts of nitrogen (0.5 to 1.5%), oxygen, and sulfur. Nitrogen is usually present in either five- or six-membered rings or as nitrile substituent. Oxygen is present as phenolic and quinone substituents, as well as in four-, five-, or six-membered rings. Sulfur is usually found in five-membered rings (McNeil, 1969). Analysis for certain metals in coal tar has revealed high concentrations of zinc (over 200 μg/g) and lead (70 to 75 μg/g); concentrations of between 1 and 10 μg/g of iron, cadmium, nickel, chromium, and copper have been found (White, 1975). Magnesium, boron and vanadium have also been identified in coal tar pitch (Liggett, 1964).

Because of the importance of pitch in various industries, a number of studies have been carried out to elucidate its structure. Most specifications for coal tar pitches include limitations of solubility in certain solvents. Different solvents are required for various specifications and the methods used vary among investigators. These differences have made it difficult to compare results (McNeil, 1966b). Table I-4 indicates several methods which may be roughly equated.

The Demann (1933) and Broche and Nedelmann (1934) methods divide the pitch into material insoluble in benzene (α-component), material soluble in benzene but insoluble in petroleum ether (β-component) and material soluble in petroleum ether (δ-component). Adam et al. (1937) extend the above methods by separating the benzene extract into soluble and insoluble portions, by adding the concentrated benzene extract to 10 times its volume of petroleum ether, and by separating the α-component into pyridine soluble (C_2) and pyridine insoluble (C_1) fractions. The petroleum ether soluble portion is referred to as "crystalloids" and the petroleum ether insoluble but benzene soluble portion is called "resinoids." Crystalloids are also defined as being soluble in hexane or similar aliphatic solvents.

Dickinson (1945) modifies the Adam method by performing a vacuum distillation on the pitch to obtain distillate oils, extracting the residue with benzene and pyridine, precipitating the benzene extract with petroleum ether and extracting the precipitate with n-hexane. Resin A is that part of the pitch soluble in n-hexane or petroleum ether; Resin B is that part of the pitch insoluble in hexane but soluble in benzene and in fractions C_1 and C_2.

A solvent analysis method (Mallison, 1950) which has been widely used in Europe divides the pitch into five fractions: H-resins, M-resins, N-resins, m-oils, and n-oils. The method is not a solvent fractionation and the fractions are not further analyzed (McNeil, 1966b). A number of other solvent analysis or fractionation methods that have been used are toluene and tetralin solvents; carbon disulfide, pyridine, benzene, petroleum ether and diethyl ether; pyridine, xylene and decalin; and nitrobenzene and acetone.

TABLE I-4. TERMINOLOGY APPLYING TO ANALOGOUS FRACTIONS AS DETERMINED BY FOUR FRACTIONATION PROCEDURES

Adam *et al.* (1937)	Dickinson (1945)	Demann (1933)	Mallison (1950)
C_1	C_1	α-Fraction	H-Resins
C_2	C_2		M-Resins
Resinoids	Resin B + some Resin A	β-Fraction	N-Resins
Crystalloids	Distillate oils + some Resin A	δ-Fraction	m-Oils and n-Oils

Source: McNeil, 1966b

TABLE I-5. MOLECULAR WEIGHT AND HYDROGEN TO CARBON RATIO OF MEDIUM-SOFT COKE OVEN PITCH

Fraction	Wt. range %	Reported mol. wt.	Av. atomic H/C ratio	Solubility
Crystalloid	45-60	258	0.67	Sol. petroleum ether
Resinoid	16-24	559	0.62	insol. petroleum ether, soluble benzene
C_2	5-15	1476	0.70	insol. benzene
C_1	3-28		0.33 to 0.46	insol. pyridine, quinoline

Source: McNeil, 1966b

To indicate the variability in these separations, the H-resin content is between 0.2 and 7.5% while M-resin content is 5.2 to 11.2% in vertical retort tars. The variations in pitches from coke ovens are H-resins 2.8 to 14.4% and M-resin 3.8 to 28.2%. The same kind of variability holds true for crystalloids (45 to 60%), resinoids (16 to 24%), C_2 (5 to 15%) and C_1 (3 to 28%) in coke oven pitch. Tars from vertical retorts contain 55 to 70% in crystalloids and less C_1 and resinoids while low temperature pitch contains less than 1% C_1 and 70 to 80% crystalloids (McNeil, 1966b).

The molecular weight and hydrogen to carbon ratio of crystalloids, resinoids, C_1 and C_2 are represented in Table I-5. The overall range in molecular weight for coal tar is between 200 and 2000. The C_1 fraction has a much lower H/C ratio. Low temperature processes are found to have higher H/C ratios. A value of 1.07 has been reported for the crystalloid fraction from continuous vertical retort pitch (Greenhow and Smith, 1960).

The distillate oil fraction has been subjected to many analyses and is the only fraction of pitch from which pure chemical compounds can be isolated by techniques normally used, such as fractionation and chromatographic separation methods. McNeil (1966b) has listed 126 compounds all boiling above 300°C (an arbitrary cut off value), most of which are condensed PAH and their heterocyclic analogs, from pitch or refined tar which is sufficiently volatile to distill without decomposition. A partial list is shown in Table I-6. PAH found in refined coal tar and in high temperature conversion process coal tar are listed in Tables I-7 and I-8, respectively.

The pitch crystalloids contain the same major components as the distillate oils. They are composed of polynuclear aromatics with an average of 3 to 6 rings and with a molecular weight in the range of 200 to 250. Compounds similar to those indicated in Table I-6 are: acenaphthene, fluorene,

TABLE I-6. COMPOUNDS IN COAL TAR PITCH OR REFINED TAR

1-Naphthylamine
2-Naphthonitrile
3-Hydroxydiphenyleneoxide
Diphenylsulfide
Carbazole
4-Hydroxybiphenyl
Phenanthridine
Acridine
Xanthene
2-Methylcarbazole
Anthracene
Phenanthrene
1-Methylfluorene
2-Azafluoranthene
13-Azafluoranthene
9-Methylphenanthrene
3-Methylphenanthrene
Pyrene
7H-Benzo(c)carbazole
7H-Benzo(a)carbazole
2-Phenylnaphthalene
Benzanthrone
Benz(a)acridine
Benz(c)acridine
Benzo(a)fluorene
Benzo(b)fluorene
Benzo(c)fluorene
3-Methylpyrene
Chrysene
Benz(a)anthracene
Tetracene
Triphenylene
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(ghi)perylene
Picene
Benzo(b)triphenylene
Dibenz(a,h)anthracene
Dibenz(a,j)anthracene
Dibenz(a,h)pyrene
Dibenz(a,i)pyrene

Source: McNeil, 1966b

TABLE I-7. PAH IN COAL TAR

PNA	Concentration (g/kg) in coal tar*	
	(1)	(2)
Anthracene	2.88	4.35
Benz[a]anthracene	6.24	6.98
Benzo[b]chrysene	0.93	0.80
Benzo[j]fluoranthene	0.63	0.45
Benzo[k]fluoranthene	1.08	1.07
Benzo[g,h,i]perylene	1.23	1.89
Benzo[a]pyrene	2.08	1.76
Benzo[e]pyrene	1.85	1.88
Carbazole	1.32	1.27
Chrysene	2.13	2.86
Dibenz[a,h]anthracene	0.30	0.23
Fluoranthene	17.7	17.8
Perylene	0.70	0.76
Phenanthrene	13.6	17.5
Pyrene	7.95	10.6

*Two samples of medicinal coal tar

Source: Lijinsky _et_ _al_., 1963

TABLE I-8. MAJOR COMPONENTS OF GERMAN HIGH-TEMPERATURE CONVERSION PROCESS COAL TAR

Component	Average weight percent
Naphthalene	10.0
Phenanthrene	5.0
Fluoranthene	3.3
Pyrene	2.1
Acenaphthylene	2.0
Fluorene	2.0
Chrysene	2.0
Anthracene	1.8
Carbazole	1.5
2-Methylnaphthalene	1.5
Diphenyleneoxide	1.0
Indene	1.0
Acridine	0.6
1-Methylnaphthalene	0.5
Phenol	0.4
m-Cresol	0.4
Benzene	0.4
Diphenyl	0.4
Acenaphthene	0.3
2-Phenylnaphthalene	0.3
Toluene	0.3
Quinoline	0.3
Diphenylenesulfide	0.3
Thionaphthene	0.3
m-Xylene	0.2
o-Cresol	0.2
p-Cresol	0.2
Isoquinoline	0.2
Quinaldine	0.2
Phenanthridine	0.2
7,8-Benzoquinoline	0.2
2,3-Benzodiphenyleneoxide	0.2
Indole	0.2
3,5-Dimethylphenol	0.1
2,4-Dimethylphenol	0.1
Pyridine	0.02
α-Picoline	0.02
β-Picoline	0.01
γ-Picoline	0.01
2,6-Lutidine	0.01
2,4-Lutidine	0.01

Source: Shults, 1975

phenanthrene, anthracene, pyrene, anthraquinone and chrysene(Hoiberg, 1965a). The more complex part of coal tar pitch (30%), represented by C_1, C_2 and resinoid fractions, appears to be a continuation of a series formed from less complex, more soluble and more volatile fractions (Table I-9), and consists mostly of ring systems not highly condensed, with the majority of the rings fused to not more than three other rings (McNeil, 1966b).

Osmotic pressure measurements have given estimates of 300 to 1000 for the molecular weight of resinoids. The oxygen, nitrogen and sulfur content is reported to be 1 to 1.5, 1.4 to 2.2, and 0.2 to 0.3 atoms per hundred atoms, respectively, indicating that this fraction is largely hydrocarbons (McNeil, 1966a).

The C_2 fraction is different from the resinoid fraction and is considered to be a complex mixture of polynuclear compounds with 5 to 20 fused rings. Carbon in the ring is the most abundant element but oxygen, nitrogen and sulfur are also present in lesser amounts. There is a fair amount of substitution, primarily methyl and hydroxy groups, the degree of methylation increases with molecular weight, and the ring structure is not highly condensed.

The C_1 fraction, pyridine insoluble material, is a black infusible powder partly soluble in quinoline, appearing to have a molecular weight range of 1500 to 2000. This C_1 fraction is highly variable and depends on the type of coal and the means of production. It is thought to consist of dispersed particles that vary from one to two micrometers in diameter. The particles absorb variable amounts of high molecular weight tar resins. Therefore quinoline extracts more of the resins from the dispersed material than does pyridine (McNeil, 1966a; Hoiberg, 1965a).

TABLE I-9. PREDOMINANT STRUCTURES IN COKE OVEN TAR

Boiling range (°C)	Average percent of tar	Major components
0-150	0.8	Single 6-membered rings Benzene Toluene Xylenes
150-200	3	Fused 6,5-ring systems Indene Hydrindene Coumarone
200-250	12	Fused 6,6-ring systems Naphthalene Methyl naphthalenes
250-300	8	Fused 6,6,5-ring systems Acenaphthene Fluorene Diphenylene Oxide

Source: McNeil, 1966a

The preliminary separations described in this section are necessary precursors to chromatographic techniques, such as gel, gas-liquid, thin layer, gravity fed column, and high performance liquid. The chromatographic methods, in conjuction with other analytical tools used to characterize and identify the compounds in pitch,will be described in detail in Chapter IV.

II - ENVIRONMENTAL EXPOSURE FACTORS: ASPHALT

A. Production and Consumption

1. Quantity produced

Asphalt sales in the United States have increased from an estimated ten million tons in 1949 to somewhat over 34 million tons in 1974 (Asphalt Institute, 1974b). Asphalt, which constitutes 9 to 75 weight-percent of crude petroleum, represented 4.7 percent of United States crude oil refinery yield in 1976, only a slight increase since 1954 (Table II-1) (Nelson, 1976).

Currently, paving represents seventy-eight percent of the asphalt market, roofing seventeen percent, and miscellaneous uses five percent (Figure II-1) (U.S. Bureau of Mines, 1975).

The consumption of cutback and emulsified asphalts has changed little since 1960, but the use of asphalt cements, which accounts for eighty percent of asphalt consumed, has increased steadily to over 22 million tons (U.S. Bureau of Mines, 1975).

Exports of asphalt were 61 thousand tons in 1972, 62 thousand tons in 1973, 75 thousand tons in 1974, and 58 thousand tons in 1975. Imports of asphalt, including native asphalts, amounted to 1.5 million tons in 1973, 2 million tons in 1974, and less than 1 million tons in 1975 (U.S. Bureau of Mines, 1975).

2. Market trends

Between 1902 and 1926, annual U.S. asphalt production increased from 20 thousand tons to 3 million tons (Asphalt Institute, 1974b). Annual production is expected to increase from the current level of 30 million tons to over 40 million tons by 1990 (Predicasts, 1976).

Under circumstances of diminished oil supplies, asphalt will be too valuable to use as a paving binder[1], and will probably be replaced by Portland

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[1] Personal communication, Walter Hubis, Gulf Mineral Resources, Denver, Colorado.

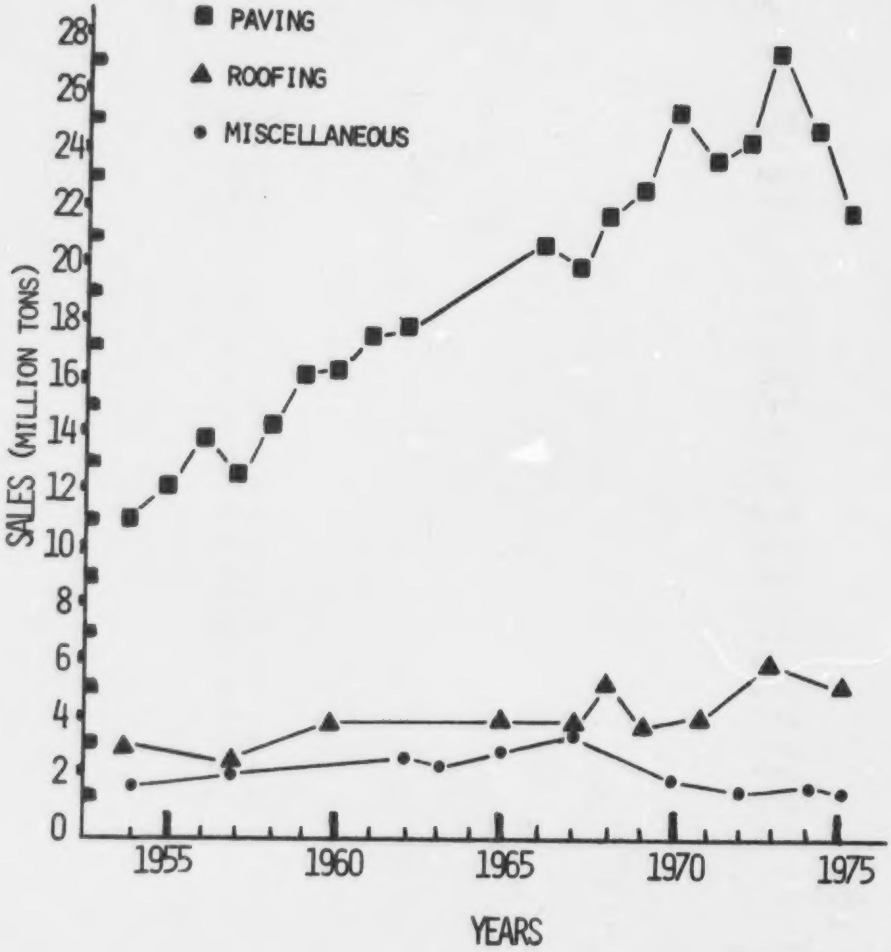
TABLE II-1
UNITED STATES ASPHALT PRODUCTION AS PERCENT OF PETROLEUM REFINERY YIELD

YEAR	% ASPHALT
1954	2.9
1955	2.9
1956	3.0
1957	---
1958	3.3
1959	3.2
1960	3.3
1961	3.4
1962	3.6
1963	3.5
1964	3.6
1965	3.7
1966	3.8
1967	3.6
1968	3.6
1969	3.7*
1970	3.6*
1971	3.8
1972	3.6
1973	3.6
1974	4.6
1975	4.4*
1976	4.7*

*Estimate

Source: Nelson, 1976

FIGURE II-1. ANNUAL DOMESTIC SALES OF ASPHALT BY MAJOR MARKETS



Source: U. S. Bureau of Mines, 1954-1976 cement-concrete, its only current competitor. The roofing market will continue to receive its share of asphalt because no competitive substitute is available (Gerstle, 1974).

With approximately six billion tons of asphalt covering roads, runways and parking lots of the United States, there may be a trend toward recycling aged asphalt. According to methods specified by Mendenhall (1976), asphalt-aggregate mixtures can be reheated and rejuvenated without impairing the penetration characteristics or weakening the material.

3. Market prices

In 1950, the price of asphalt was nineteen dollars per ton. Until the early 1970's, the price per ton fluctuated between seventeen and twenty-one dollars. Between 1970 and 1974, the price increased to twenty-eight dollars per ton and is expected to continue increasing (Krchma and Gagle, 1974).

4. Producers and distributors

On January 1, 1975, there were 287 crude oil refineries in the United States with a combined distillation capacity of 15.4 million barrels per day. Of these, 121 refineries produced asphalt (U.S. Bureau of Mines, 1976). Economic considerations dicatate whether a petroleum residue will be processed as an asphalt product, heavy fuel oil or petroleum coke, or burned as fuel (Lewis, 1965).

The period of greatest asphalt consumption occurs from July through October, with August as the month of greatest usage. Because production usually cannot meet demand during the peak season, asphalt is often stockpiled at the refinery or at bulk terminals which have been established to facilitate distribution to sites of paving and roofing material manufacture (Lewis, 1965). Asphalt is shipped from the refinery or bulk terminal by truck, barge or rail car.

5. Production methods

Ninety-eight percent of asphalt used in the United States is derived from crude oil (Miles, 1977), although not all crudes are good, or even adequate, sources of asphalt. In general, if a crude contains a residue (fraction boiling above 399°C (750°F)) that has an API gravity below 35 and a Watson characterization factor of less than 11.8 (i.e., more naphthenic than paraffinic), it may be adequate for asphalt manufacture (Gary and Handwerk, 1975).

The following information concerning processes for the recovery and refining of asphaltic residues is based on discussions by Jones (1973), Gary and Handwerk (1975), Corbett (1966), Ball (1965), Broome (1973), Sterba (1974), Thornton (1974), Oglesby (1975) and the Asphalt Institute (1973, 1974b).

The United States petroleum industry makes 2,347 products, of which 209 are asphalts (Table II-2) (Mantell, 1975). Asphalts from different crude oil stocks may vary inherently in properties such as temperature susceptibility (the amount of change is viscosity with change in temperature). Properties such as durability may also be altered appreciably by processing treatment and addition of fluxing oils or blending stocks.

In the refining of petroleum, crude oil is first distilled at atmospheric pressure at temperatures up to 300° to 400°C (572° to 752°F) in order to separate it into intermediate fractions of specific boiling ranges. After lower boiling fractions such as gasoline, kerosine, and diesel oil are removed, the remaining "reduced" crude, or straight-run residue, is further distilled under vacuum to separate gas oil and lubricating oil sidestreams. The residue withdrawn from the vacuum tower may become propane deasphalting stock or be mixed with additional atmospheric residue for further distillation under vacuum. Sidestreams from this third distillation may be used as catalytic cracking feedstocks, while the

TABLE II-2. PRODUCTS MANUFACTURED BY U.S. PETROLEUM INDUSTRY

Class	Number
Asphalts	209
Carbon blacks	5
Chemicals, solvents, misc.	300
Cokes	4
Distillates (diesel fuels & light fuel oils)	27
Fuel gas	1
Gasolines	40
Gas turbine fuels	5
Greases	271
Kerosines	10
Liquefied gases	13
Lubricating oils	1,165
Residual fuel oils	16
Rust preventives	65
Transformer and cable oils	12
Waxes	113
White oils	100

Source: Mantell, 1975

asphaltic residue is removed from the tower bottom. Steam may be used during any of these distillation steps in order to improve vaporization and minimize coke formation in the apparatus.

Propane deasphalting is a process for removing resins or asphaltic components from a viscous hydrocarbon fraction in order to recover lube or catalytic cracking stocks. The charge for solvent deasphalting is derived from atmospheric or vacuum distillation bottoms that are low in asphalt content. The process consists of a countercurrent liquid-liquid extraction under temperatures and pressures determined by the nature of the charge stock. The deasphalted oil solution is withdrawn from the tower top and the propane solvent is stripped and recycled.

Asphalt may be subjected to some form of thermal cracking which breaks heavy oil fractions into lighter, less viscous fractions by applying heat and pressure in the absence of a catalyst. Coking, or delayed coking, is a severe form of cracking, at temperatures exceeding 1090°C (2000°F), which converts a heavy residue into a weak coke suitable for use in the manufacture of carbon electrodes but not in metallurgical blast furnaces. Visbreaking, at temperatures ranging from 475° to 525°C (887° to 977°F), is a relatively mild treatment that results in little boiling point reduction but greatly lowered viscosity. Neither coking nor visbreaking yields asphaltic residues as does "thermal cracking," a process now supplanted by catalytic cracking for the production of gasoline (Corbett, 1966). Thermal asphalts result from a cracking process in which a heavy oil stock is heated to 480° to 590°C (900° to 1100°F), then discharged into a reaction vessel under pressures up to 200 psig. The cracked products are distilled, leaving an asphaltic residue (Figure II-2).

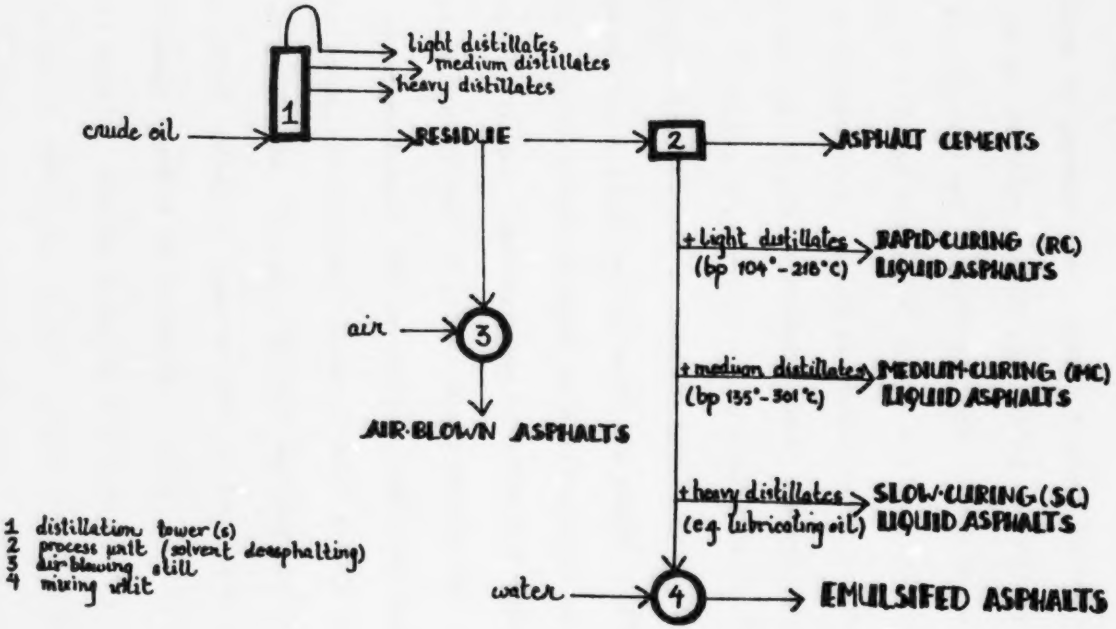

crude oil
1
light distillates
medium distillates
heavy distillates
RESIDUE
2
ASPHALT CEMENTS
+ light distillates (bp 104°-218°C)
RAPID-CURING (RC) LIQUID ASPHALTS
+ medium distillates (bp 135°-301°C)
MEDIUM-CURING (MC) LIQUID ASPHALTS
+ heavy distillates (e.g. lubricating oil)
SLOW-CURING (SC) LIQUID ASPHALTS
air
3
AIR-BLOWN ASPHALTS
water
4
EMULSIFED ASPHALTS
1 distillation tower(s)
2 process unit (solvent deasphalting)
3 air blowing still
4 mixing unit

FIGURE II-2. REFINERY STEPS IN THE PRODUCTION OF ASPHALT

Straight-run asphalts may be "air-blown" in order to produce specification products with reduced volatile content and increased melting point (relative to the straight-run stock). The stock is preheated to 200° to 280°C (392° to 536°F) and air is forced through the hot flux at rates ranging from 15 to 50 cubic feet per minute per ton of asphalt charge. Air blowing is occasionally done in the presence of phosphorus pentoxide, ferric chloride or zinc chloride in order to shorten blowing time. The addition of the essentially non-recoverable "catalyst" in concentrations from 0.1 to 3 percent results in a product with higher penetration for a given softening point. High ductility and improved temperature susceptibility are other advantages which lead to the use of "catalytic asphalts" in a variety of specialty base stocks.

Asphalt cements make up eighty percent of the current asphalt market (U.S. Bureau of Mines, 1975). These are penetration grade asphalts derived from residua of either vacuum distillation or propane deasphalting. They may be air blown and may represent a mixture of base stocks. Asphalt cements, cut back with a petroleum solvent, are either rapid-curing or medium-curing asphalts. Road oils (slow-curing) are the least uniform of the liquid asphalts and may in fact be directly distilled rather than cutback. Asphalt emulsions are normally produced from 180-200 penetration asphalt cements. Depending on their intended use, asphalts may be liquefied in various ways (Oglesby, 1975; Day and Herbert, 1965; Mertens and Borgfeldt, 1965). Blending of cutback asphalts and emulsified asphalts is not necessarily a refinery process (Figure II-2).

Diluting an asphalt cement with a lighter petroleum distillate yields a product with lower viscosity. Upon evaporation of the solvent, the cured asphalt has approximately the same penetration grade as its parent asphalt cement. The base stock may be directly blended or stored in tanks which range in size from 25,000 to 100,000 barrels. The stock is delivered to a blend tank and mixed with a measured volume of diluent.

Rapid-curing cutbacks (RC) contain a diluent (gasoline or naphtha type) with a boiling range of 104° to 218°C (220° to 425°F). The base asphalt will vary from 70 to 100 penetration in order to leave a cured asphalt of 80-120 penetration. The least viscous grade (RC-70) can be poured at room temperature.

Middle-curing cutbacks (MC) use a kerosine type diluent with a boiling range of 135° to 302°C (275° to 575°F). This cutback is more versatile than the others, with good wetting properties on fine aggregates and a moderate evaporation rate. The base asphalt will vary from 70 to 250 penetration to leave a cured residue of 120 to 250 penetration. MC-30 and MC-70 can be poured at room temperature. MC-70 can contain as much as 40 percent by volume diluent. The most viscous grade, MC-3000, may have as little as 18 percent solvent and usually must be warmed before use.

Slow-curing asphalts (SC), often referred to as "road oils," may be refined directly to grade rather than consisting of an asphalt cement plus diluent. They are the least uniform in composition. Heavy diesel fuel, overhead gas oils or cycle stocks from other processes may be used as solvents. The lightest grade (SC-70) has the consistency of light syrup. The heaviest grade (SC-3000) will scarcely deform at room temperature, and is slightly less viscous than the softest asphalt cement (200 to 300 penetration).

Aqueous emulsions in which the asphalt content is 55 to 70 percent by weight are another form of liquefied asphalt. The three emulsion grades - rapid-setting, medium-setting, and slow-setting - can be applied at normal temperatures. The asphalt cures by evaporation of the water rather than of a petroleum solvent, thus avoiding hydrocarbon emissions. Emulsions can be applied on wet aggregates and generally are ready to resist traffic damage sooner than cutbacks. The equipment needed for mixing and application is simpler and less expensive than that required for other asphalt products.

Before 1957, anionic emulsions were the only type commercially available. Saponified fatty and resinous acids or saponified tallow derivatives were the emulsifying agents used with an asphalt cement of 180 to 200 penetration. Cationic emulsions, using a quaternary ammonium compound as an emulsifying agent, are now available and can be used with a wide variety of mineral aggregates. They adhere well to wet aggregates, and can be used under conditions of high humidity or low air temperatures.

B. Uses

Asphalt is a readily adhesive, highly waterproof, durable thermoplastic material, resistant to the action of most acids, alkalis and salts. These properties are utilized in a wide variety of applications.

1. Major uses

a. Paving

(1) Production and consumption

The Standard Industrial Classification (SIC) category SIC 2951 includes 964 establishments manufacturing asphalt (in some cases, coal tar) paving mixtures as well as blocks of asphalt, coal tar, or creosoted wood. Of these 964, 889 had seventy-five percent specialization (defined as the ratio of all primary products to the total of primary plus secondary products). About 10,000 production workers are classified under SIC 2951 (U.S. Bureau of Census, 1975) (Table II-3). The top ten paving mix producers according to 1974 production figures are listed in Table II-4.

The value of all paving mixtures and blocks shipments classified under SIC 2951 was $265.9 million in 1950, $561.9 million in 1968 and $893.4 million in 1972. The amount of asphalt of less than 200 penetration consumed in 1967 by

TABLE II-3. EMPLOYMENT SIZE OF ESTABLISHMENTS (SIC 2951)
PAVING MATERIALS

Total	964
Establishments with an average of--	
1 to 4 employees	347
5 to 9	286
10 to 19	163
20 to 49	117
50 to 99	34
100 to 249	13
250 to 499	2
500 to 999	1
1000 to 2,499	1

Source: U. S. Bureau of Census, 1975

TABLE II-4. THE TOP TEN PAVING MIX PRODUCERS: 1974

Producer and home state	Plant mix tonnage
The General Crushed Stone Co., Pa.	1,500,000
L.M. Pike & Sons, Inc., N.H.	1,334,545
The Interstate Amiesite Corp., Pa.	1,000,000
Asphalt Products Corp., S.C.	989,000
Broce Construction Co., Okla.	847,214
Associated Sand & Gravel Co., Inc., Wash.	843,110
Ajax Paving Industries, Mich.	800,000
Western Engineering Co., Ia.	800,000
Dickerson, Inc., N.C.	750,000
Highway Materials, Inc., Pa.	750,000

Source: Roads and Streets, 1975

the paving industry was 4,761,400 tons with a delivered cost of $104.5 million. In 1972, 5,410,000 tons were consumed at a cost of $157.9 million (U.S. Bureau of Census, 1975).

(2) Materials

Currently, ninety-four percent (over 1.7 million miles) of the paved surfaces in the United States are bituminous (Oglesby, 1975). These bituminous surfaces range from dirt surfaces lightly sprayed with liquid asphalt to high-grade asphalt cement pavements.

A finished paving mix consists of about six percent asphalt cement and ninety-four percent mineral aggregates. In addition to asphalt cement, a variety of cutback and emulsified asphalts are used to treat or finish roads (See Section II.A.5. for descriptions of asphalt cements, cutbacks and emulsions). Approximately 700 million tons of mineral aggregates are consumed annually for all aspects of highway construction. Slag, broken stone, gravel and sand, the aggregates most commonly used, constitute 75% by volume of a finished paving mix. Because aggregates vary greatly in composition, strength, porosity and surface roughness, specifications and tests have been developed to insure certain minimum standards (Oglesby, 1975).

Experimental pavements using asphalt-rubber mixtures have been laid in many states. Rubber enhances the coefficient of friction, improves the stability of paving mixtures, and reduces temperature susceptibility and brittleness, as well as imparting greater elasticity and extending pavement life (Oglesby, 1975). Other experimental pavements have been laid using an epoxy resin and asphalt binder which is resitant to wear, heat and the solvent effects of fuel (Hoiberg, 1965).

(3) Process descriptions

Hot mix plants

General information in the following section was obtained from Oglesby (1975).

Although road surfaces can be treated with either hot or cold applied asphalt, hot treatments are the most common. It is estimated that there are 4500 paving plants of all sizes in the United States; plants with a capacity of 600 tons per hour of finished mix are common near most large cities (Puzinauskas and Corbett, 1975).

Asphalt is loaded at the refinery or bulk terminal at elevated temperatures into steam heated tank cars, trucks or drums and transported to the hot mix plant. The asphalt, stored in large heated underground tanks, can be pumped directly to the platform on which finished asphalt-aggregate mixtures are produced.

The mineral aggregates are sent through the drier, a firebrick lined steel cylinder, to drive off moisture and heat to a mixing temperature of 149° to 160°C (300° to 320°F). The hot aggregates are segregated by size through shaking screens.

In batch-mixing processes (the most common), aggregates and the asphalt binder are mixed by revolving blades in pug mills that can reach capacities of sixteen tons or more. The finished mix is deposited into waiting trucks and taken to the job site.

High capacity plants use a process whereby hot binder is introduced directly into the drier, thus insuring continuous output of finished product. Exposure of the binder to drier conditions does not seem to accelerate its aging, and the problem of dust from fine aggregates is substantially reduced.

Cold mix plants

Cold mix plants are similar to hot mix plants in operation, except that the aggregates are cooled before being coated with a naphtha liquefier. The coated aggregates are mixed with hot asphalt binder to form the finished paving product. Such cold mix products are not in common use.

Paving

In the past, all placing and leveling of hot asphalt was performed manually. Self-propelled finishing machines have largely supplanted manual operations, although small jobs, especially patching operations in cities, still rely on hand equipment. The hot aggregate-asphalt mixture, which is transported to the job site in dump trucks, is unloaded, spread and tamped, usually with one machine. Final tamping is done by large, smooth-wheeled rollers.

Road mix processing, still used on side roads, is performed with a single machine that picks up aggregates, either freshly laid or pulverized from the old surface, mixes them with asphalt cement and spreads the new pavement.

Surface treatment

Road surfaces are treated with a pressurized distributor truck (800 to 5500 gallon capacity) from which liquid asphalt is forced through a spray bar approximately twenty feet long.

Several types of surface treatments may be used:

1) Dust palliatives: light slow-curing road oil or slow-setting emulsions applied at 79°C (175°F).

2) Prime (tack) coats: light medium-curing cutbacks or light road tar or slow-setting emulsions.

3) Armor coats on macadam or low quality concrete: varies with surface

4) Seal coats: Sand or crushed stone mixed with a slow-setting road oil applied to damp pavement. Slow-setting emulsions are sprayed on to rejuvenate surfaces.

Proper temperatures of application, as well as ambient temperature, are fundamental to good asphalt performance. State highway departments specify minimum air temperatures for laying asphalt ranging from 0°C (32°F) to 15.6°C (60°F), the usual being 4.4°C (40°F). (Table II-5).

b. Roofing

(1) Production and consumption

In 1972, there were 236 plants in classification SIC 2952; which includes establishments that manufacture asphalt and coal tar saturated felts in roll or shingle form, as well as roofing cements and coatings (U.S. Office of Management and Budget, 1972). Of the total 236, 215 had seventy-five percent or more specialization (U.S. Bureau of Census, 1975). (Specialization is defined as the ratio of all primary products to the total of primary plus secondary products). There were 11,500 production workers classified under SIC 2952 in 1972 (U.S. Bureau of Census, 1975) (Table II-6).

Illinois, California, Texas, New Jersey, Ohio and Pennsylvania each have over ten roofing plants. Total sales of the plants in these states in 1973 were $474 million; total sales for the United States were $881 million (Gerstle, 1974).

The value of all shipments of asphalt and pitch roofing "coatings and cements" (SIC 2952-2) was $67.9 million in 1958, $124.5 million in 1968 and $155.3 million in 1972 (U.S. Bureau of Census, 1975). The value of all shipments of asphalt and pitch "roofing and siding" products (shingles, felt rolls)

TABLE II-5. SUGGESTED MIXING AND APPLICATION TEMPERATURES FOR ASPHALTIC MATERIALS

Type and grade of material	Pugmill mixing temperature		Spraying temperature (surface treatment)	
ASPHALT CEMENTS	°C	°F	°C	°F
40/50	134-177	275-350	149-210	300-410
85/100	124-163	255-325	143-204	290-400
200/300	107-149	225-300	134-196	275-385
CUTBACK ASPHALTS				
RC,MC,SC				
70	35-60	95-140	49-107	120-225
800	74-96	165-205	93-169	200-305
3000	93-116	200-240	113-119	235-245
EMULSIFIED ASPHALTS				
MS-2 CMS-2	10-77	50-170	38-71	100-160
SS-1 CSS-1	10-77	50-170	24-54	75-130

Source: Oglesby, 1975

TABLE II-6

EMPLOYMENT SIZE OF ESTABLISHMENTS (SIC 2952) ROOFING MATERIALS

Total	236
Establishments with an average of--	
1 to 4 employees	33
5 to 9	26
10 to 19	36
20 to 49	52
50 to 99	31
100 to 249	50
250 to 499	6
500 to 999	2

Source: U.S. Bureau of Census, 1975

(SIC 2952-3) was $313.6 million in 1958, $385.9 million in 1968 and $690.6 million in 1972 (U.S. Bureau of Census, 1975).

In 1967, manufacturers classified under SIC 2952 consumed 9.1 million barrels of 200 and less penetration asphalt; by 1972, consumption increased to 12.8 million barrels. Consumption of 200 and over penetration asphalt was 27.6 million barrels in 1967 and 41.1 million barrels in 1972 (U.S. Bureau of Census, 1975).

Although coal tar and coal tar pitch are still used in the roofing trade, there has been a trend of increasing use of asphalt. For example, 864,000 tons of asphalt saturated felt were shipped in 1967, compared to 46,000 tons of tar saturated felt; in 1972, asphalt felt shipment increased to 871,500 tons, while shipments of tar saturated felt declined to 36,500 tons (U.S. Bureau of Census, 1975).

(2) Products and materials

The information in the following section was obtained from Gerstle (1974) and Berry (1968).

Bitumens (asphalt or tar), fillers or mineral coatings, and felts or woven fabrics are the three major raw material classes used in the "asphalt" roofing industry. Major products include roll roofing, siding, shingles, saturated felts, and bituminous adhesives and cements.

Roofing grade asphalts are air blown to certain softening point specifications. The normal range of softening points for saturant grade asphalts is 38° to 60°C (100° to 140°F), for roofing cements 63° to 82°C (145° to 180°F), and for coating grade asphalt 93° to 107°C (200° to 225°F).

Mineral granules such as sand or asbestos used on felt rolls and cut shingles must be dust-free, opaque to sunlight and bondable to the asphalt coating. Approximately 700 pounds of granules are used per ton of finished material.

Felts of cloth, paper or asbestos are formed on machines similar to those used in the manufacture of paper. Woven fabrics such as burlap, hessian or duck are also used; these materials, however, do not take up as much saturant as pressed felts.

Bituminous adhesives are used on built-up roofs subjected to wide temperature fluctuations and in construction of above or below ground membrane waterproofing on bridges, culverts, tunnels or foundations. Asphalt putty or bituminous cements are prepared to troweling consistency and are used for repair of metal and composition roofing, for damp proofing and minor waterproofing.

(3) Process descriptions

The following section is based on information from Berry (1968) and Gerstle (1974).

Composition roofs are either "built-up" or "prepared." Built-up roofs are essentially manufactured on the job, assembled by alternating layers of asphalt or tar saturated felt and soft bitumen. Shingles are considered "prepared" roofing. Both types of roofs consist of a structural felt saturated with bitumen and finished with a hard bitumen coating embedded with mineral granules.

Prepared roofing material

Production of saturated felt to wind in rolls or cut into shingles is the primary operation of roofing mill processes.

Standard weight felts (15, 30, and 55 pounds per 48 square feet) are run through saturator tanks filled with hot asphalt (232° to 260°C (450° to 500°F)) on loopers running at average speeds between 250 and 400 feet per minute.

Saturation with hot bitumen fills voids in the felt, binds the fibers, and primes the material for an outer protective coating.

After cooling and drying, the saturated felt is coated with a bitumen relatively harder than that used in saturation. If smooth roll roofing is being manufactured, the saturated felt or fabric is covered with a parting agent such as talc, mica, slag or sand (approximately 3 to 5 pounds per 100 square feet of felt) which is applied to facilitate separation of layers. Mineral granules are embedded into the top coating with hot press rollers (107° to 135°C (225° to 275°F)). A parting agent is applied to the back and the material is either rolled or cut into shingles.

Built-up roofing

Large, low-slope roofs on buildings such as warehouses and large apartment complexes are often built up. The roof is assembled using bitumen-saturated felt and cold-process cement or roofing asphalts having a softening point of 57° to 93°C (135° to 200°F).

Hot-applied systems utilize alternating layers of standard roofing felt and bitumen. The bitumen is usually in solid blocks that must be chopped and heated. The first layer of felt is spread and mopped with hot bitumen. Depending on the size and complexity of the job, subsequent layers are placed manually and sealed or put down with a felt machine that spreads heated bitumen and rolls out felt in a single operation.

A prefabricated cap sheet (felt-surface with mineral granules) is laid, or the granules may be embedded on site using an asphalt spreader followed by a rock spreader.

Cold-applied roofing materials are used when the standard heating kettle of hot-applied systems is dangerous or impractical. The cold-process cement adheres to the felt and the cement solvent (usually a 149° to 204°C (300° to 400°F) boiling range naphtha) evaporates through it. Within 24 hours of assembling, the roof is waterproof.

2. Minor uses

The following section is based on information obtained from Hoiberg et al. (1963), Hoiberg (1965a,b) and Asphalt Institute (1973, 1974a).

The value of asphalt in waterproofing, cementing, and providing protective coatings has been known at least five thousand years. In the Mesopotamia and Indus Valley regions (ca 3500 BC) asphalt was used for paving, building, as a wood protectant and in waterproofing enclosures. The Egyptians used asphalt in mummification.

The uses today classified as "minor" or "miscellaneous" are nonetheless significant, both in terms of value and diversity.

Asphalt is compatible with a variety of fillers. Styrene-butadiene rubber, tire buffings, neoprene and reclaimed rubber have all been used in mixtures with asphalt to produce caulking compounds, joint sealants, cable coatings, shoe soles, and sound insulation panels, as well as paving mixes. Asphalt and polyepoxides (polyglycidal ethers) produce mixtures of excellent chemical and solvent resistance. Pavements, surface treatments, and protective coatings for tunnels and bridge abuttments are often asphalt-epoxy mixtures. Polyvinyl chloride, methacrylic resins, polybutenes and polybutadienes, coumarone resin and mineral rubber (gilsonite) are other additives that improve the performance of asphalt.

Asphalt compounds are widely used in hydraulic engineering and erosion control. In conjunction with highway construction and maintenance, both asphalt and coal tar pitch are used for soil stabilization and bank erosion control. Dam linings and sealants, canal linings and sealants, catchment basins, dike protection, levee stabilization, ditch linings, sand dune stabilization, sewage lagoons, swimming pools and waste ponds are other applications for asphalt in hydraulic engineering.

Asphalt has a variety of uses in the construction trade: building blocks, bricks, sidings, floor tiles, insulation, putty, damp proofing, varnishes, plumbing pipe coatings, paint compositions, joint fillers and building papers.

Because of its low electrical conductivity, asphalt is utilized in such products as insulating tapes, wire coatings, transformer potting compounds, capacitor seals, molded conduits and battery sealants.

Asphalt is an effective sealant for containing wastes of low or intermediate radioactivity (Christenson, 1968).

Bitumens have been used as a stable matrix to which fertilizers, pesticides and rodent repellents are added for slow release uses in fields, road banks or on trees.

Other products in which asphalt may be found are clay pigeons, foundry cores, graphite and electrode binders, linings for burial vaults, embalming compositions, printing inks, paper water proofing, tree paints, mulches, automobile undersealants, briquette binders, marine enamels, mirror backings and imitation leather.

3. Alternatives to the use of asphalt

Currently the paving industry is dominated by asphalt: ninety-four percent of the paved roads in the United States are covered with asphalt; only six percent with Portland cement-concrete (PCC) (Oglesby, 1975). Often highways of PCC are laid, then paved with asphalt when resurfacing is required[1]. Coal tar pitch is also available as a replacement for asphalt in paving binders.

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[1] Personal communication, Ralph Cannon, U.S. Occupational Safety and Health Administration, Cincinnati, Ohio.

Although the current roofing market is dominated by asphalt products, there are widely used substitutes. Pitch has been used for years and has, from an engineering standpoint, performed well; materials such as sheets of neoprene, silicone rubber, polyvinyl chloride, polyvinyl fluoride, chlorosulfonated polyethylene and ethylene polypropylene terpolymers have received attention as potential roofing products. Liquid forms of some of these materials have been used with glass fiber mats, polymer bonded asbestos felt and polyurethan foam. Metal roofs of galvanized iron or corrugated aluminum have been used in the South. Slate, tile and wood shingles have had periods of popular use. Asbestos-cement, formed of long asbestos fibers, portland cement and fine silica, is a durable, low maintenance roofing that was popular in the middle nineteenth century.

The tar from plastics pyrolysis has a much lower PAH content than asphalt and can be fashioned into a good, serviceable substitute for asphalt (Baum and Parker, 1974). How much work is being done in this area is uncertain.

Other than coal pitches, which may increase in availability as petroleum supplies diminish and coal conversion is expanded, a universal replacement for asphalt will probably not be found. Faced with choices of substitutions, the versatility and overall value of asphalt, known for over 5000 years, is apparent.

C. Environmental contamination potential

1. Controlled and uncontrolled emissions

a. Air blowing

Of seventy-six roofing companies surveyed by the Midwest Research Institute, 82 percent purchased asphalt air blown at the refinery. The thirteen companies that processed their own asphalt all had thermal afterburners (fume incinerators) as air pollution control devices. Refinery air blowing operations, by and large, also have some variety of fume incinerator as a control device (Gorman, 1976).

At one time, blowing was done primarily in horizontal cylindrical tanks (stills). The conversion to vertical tanks has resulted in reduced emissions because of the shorter blowing time required. Losses of asphalt from horizontal stills have been estimated from 3 to 5 percent of the total amount blown; losses from vertical stills are between 1 and 2 percent (Gerstle, 1974).

Rate of air flow, temperature, phase of the blowing cycle, sulfur content of the asphalt, softening point of the asphalt and duration of the operation all influence overall emissions. A high-melting asphalt, for example, requires a longer blowing time, thus producing a greater amount of particulate emissions.

Air blowing emissions may contain water vapor, carbon monoxide, carbon dioxide, sulfur and nitrogen oxides, hydrogen sulfide, aldehydes, entrained asphalt droplets and polycyclic aromatic hydrocarbons (Kratky, 1968; Jones, 1973; Gerstle, 1974).

About 0.0008 to 0.0019 percent of the particulate emissions may consist of PAH (Gerstle, 1974). PAH isolated from air blowing emissions include benzo(c)-phenanthrene, benzo(a)pyrene, benzo(e)pyrene, 7,12-dimethylbenz(a)anthracene, dibenz(a,h)pyrene, dibenz(a,i)pyrene, pyrene, anthracene, phenanthrene and fluoranthene (Gerstle, 1974;von Lehmden *et al*., 1965).

Emission control

The primary method of control for air blowing operations is the thermal afterburner (fume incinerator). For optimal operation the effluent gas should be retained in the incineration chamber from 0.3 to 0.5 seconds. For 90 percent control the minimum chamber temperature should be 750°C; 99 percent control can be achieved with a chamber temperature of 816°C (Jones, 1973; Gerstle, 1974). Afterburners in operation currently raise temperatures from 538°C to 1090°C (Gorman, 1976).

Afterburners may be used in conjunction with scrubbers. In this case, the effluent from the afterburner flows through an oil-water gravity separator and then to the scrubbing unit. The oil may be removed and burned as fuel or reprocessed (Jones, 1973). The gases from the scrubber are vented to the atmosphere.

Several other control methods are potentially available to contain emissions from asphalt airblowing. Catalytic fume burners are not recommended because entrained asphalt droplets in the effluent gas clog the catalyst (Jones, 1973; Gorman, 1976). Dry electrostatic precipitators are also difficult to maintain because asphalt droplets foul the filters (Gerstle, 1974; Gorman, 1976). Wet electrostatic precipitators can give 99 percent control; however, the water must be processed before disposal (Gerstle, 1974; Gorman, 1976). High energy air filters are unable to control gaseous emissions or odors but can collect 98 percent of the particulate emissions and are easy to maintain (Gorman, 1976).

b. Roofing mills

Forty-eight percent of roofing plants (SIC 2952) are located in cities with populations of over 100,000; the six largest plants account for 20 percent of the total production of roofing materials. Poorly controlled emissions thus could contribute to the general air pollution burden of many urban areas (Gerstle, 1974).

Asphalt roofing plants are often characterized by a hazy, odorous atmosphere in and around the plant, Unless air blowing (see preceding section) is done at the plant, the major source of emissions is the saturator tank. Sulfur compounds, aldehydes, carbon monoxide, water vapor, gaseous hydrocarbons and entrained asphalt droplets are usually present. PAH may be a problem from the saturator tank or the hot asphalt storage tanks. Inorganic particulates from the sand (mineral granule) drier, the coating mixer or application of the parting agent commonly contribute to the hazy atmosphere (Gerstle, 1974).

The saturator tank is ordinarily somewhat enclosed by a hood, which may vent directly to the atmosphere or to a control device similar to those used for air blowing emissions. If particulate emissions are present, fabric filters can be installed (Gorman, 1976).

Roofing kettles

Thermal cracking caused by hot spots in roofing kettles (reaching 538°C near the blast burners) is responsible for the dense white vapors that are often associated with roofing operations. According to a study by Thomas and Mukai (1975), maintaining an even kettle temperature of less than 260°C will eliminate all apparent emissions. The study recommends that granular asphalt be introduced into the kettle through an interlock system, rather than removing the kettle lid, and that an afterburner (fume incinerator) be installed on the exhaust duct.

c. Hot mix plants

There are approximately 4500 hot mix plants in the United States, producing 350 million tons of finished paving mix annually (Puzinauskas and Corbett, 1975). These plants contribute over 31 thousand tons of particulates to the atmosphere each year. This represents less than 0.01 percent of the nation's particulate inventory (Pit and Quarry, 1972). The major source of particulate emissions from hot mix plants is the aggregate drier; quantities up to 6700 pounds per 182 tons of finished mix have been reported. Combined particulate emissions from other sources - aggregate elevators, aggregate separating screens and pugmill mixers - are three or four times less (Danielson, 1973).

Entrained particulate material in the uncontrolled effluent gas stream may represent four to eight percent of the weight of the mineral aggregate being dried (Pit and Quarry, 1972). When mineral filler 74 micrometers or less in diameter is being dried, up to 55 weight-percent of the material may be lost *to the effluent gas* stream (Danielson, 1973). Particulate matter in the uncontrolled emissions ranges up to 100 µm in diameter, with almost 70 percent by weight associated with particles less than 74 µm and 20 percent with particles less than 5 µm (U.S. Environmental Protection Agency, 1975a).

Hot mix plant exhaust gases that meet federal air pollution standards contain few particles larger than 40 µm; the majority range in size from 0.1 to 10 µm (U.S. Environmental Protection Agency, 1975a).

In addition to particulates, emissions from hot mix plants can contain carbon monoxide, nitrogen oxides, sulfur dioxide, hydrogen sulfide, carbonyl sulfide, aldehydes, phenol, polycyclic aromatic hydrocarbons and metals (Puzinauskas and Corbett, 1975). PAH isolated include pyrene, benz(a)anthracene, anthracene, benzo(a)pyrene, benzo(e)pyrene and perylene (Puzinauskas and Corbett, 1975; von Lehmden et al., 1965).

Metals in asphalt tend to remain associated with the high molecular weight, relatively nonvolatile organic complexes; thus they can be expected to remain in the finished mix. Low concentrations, however, of cadmium, lead, nickel, and vanadium have been detected in asphalt plant emissions (Puzinauskas and Corbett, 1975). In a study by Klein (1972) an "asphalt plant" (unspecified products) was implicated as the source of mercury, at levels ranging from 0.15 to greater than 0.3 ppm, found in the soil of an area of woodlands and fruit orchards.

Control methods

The federal standards for asphalt hot mix plants (40 CFR 60.11) limit particulate emissions to less than 90 milligrams per dry standard cubic meter (mg/dscm) and opacity to less than 20 percent (U.S. Environmental Protection Agency, 1974).

The collection efficiency of most cyclone systems used for control of hot mix plant effluent gases varies from 70 to 90 percent for most particle sizes (Danielson, 1973). A wet scrubber (centrifugal or high energy wet venturi) or fabric filter can be added to the cyclone sytem to increase control efficiency up to 99 percent (Danielson, 1973). Water from the scrubbers may be contaminated with mineral particles (less than 74 μm), clay particles, sulfuric acid (depending upon type of fuel used to fire drier), gasoline, oil or asphalt (Asphalt Institute, 1974 b).

d. Paving

Preparation of cutback asphalts and conditions of use have been discussed in Sections II.A.5. and II.B.1.a.(3).

Approximately four percent - 655,000 metric tons - of the volatile organic compounds emitted annually from all U.S. stationary sources have been attributed to the use of cutback asphalts. Although the mixing and transporting of liquified asphalts contributes to emissions, road surfaces are the major source. It has been estimated that substitution of emulsified asphalts (water and asphalt) would reduce volatile organic compound emissions from paved surfaces by 100 percent. States that have begun substituting emulsions for cutbacks have reported few problems or major expenses associated with the transition. No significant solid or liquid wastes result from usage of emulsions (U.S. Environmental Protection Agency, 1977; Kandahl, 1974).

2. Contamination potential of asphalt transport and storage

There are no available estimates of the actual or potential contamination from the transport of asphalt or its products. According to 1972 figures, over 70 percent of asphalt paving and roofing products, solid and liquid, are shipped distances between 300 and 999 miles. Of that percentage, 65 percent are loads exceeding 45 tons shipped primarily by water, secondarily by rail. More than 20 percent of asphalt loads are 15 to 30 tons shipped by truck (U.S. Bureau of Census, 1976). Liquid asphalt is shipped in specially designed trucks, heated rail cars or barges.

There are few estimates of contamination potential due to storage of asphalt. Liquid asphalt is maintained in tanks of various sizes at temperatures of 178° to 232°C (350° to 450°F). Emissions are variable and depend, in part, on storage temperature, asphalt composition and frequency of filling. Recently constructed tanks minimize hydrocarbon emissions and, although many are vented to the atmosphere, some are attached to thermal afterburners (fume incinerators) (Gerstle, 1974).

Samples of vapors displaced during a filling operation of hot storage tank showed nitrogen (67.3%), oxygen (13%), carbon monoxide (1.4%), water (18.2%) and traces of methane, ethane and argon. An estimate of possible hydrocarbon displacement, assuming a molecular weight of 120, is 0.01 pounds of hydrocarbon per ton of asphalt (Gerstle, 1974).

3. Contamination potential from disposal

How much asphalt is actually "thrown away" is not known. According to Mantell (1975), asphalt containing oil bottoms or not meeting specifications is buried in gulleys or landfill areas.

Much of the refinery waste of 20 or 25 years ago is now being processed into marketable goods or has been eliminated by alternative processes. Waste that is generated is still most commonly buried in landfill areas. Quality control of these operations is variable, depending upon the individual circumstances (Rosenberg et al., 1976).

The most tangible contribution of asphaltic residues to the environment is metals or organometallic complexes. Metals potentially present in asphalt waste are vanadium, nickel, iron, copper, small amounts of cadmium, cobalt, lead, molybdenum and mercury. An estimate of contamination by these metals from waste asphalt is not available (Rosenberg et al., 1976).

4. Environmental contamination potential from use

Large surface areas of asphalt remain constantly exposed to the environment. Aside from emissions and effluents from the manufacture of asphalt products, many uses provide potential sources of contamination: roads, soil and shoreline stabilizers, weatherproof coatings on foundations, tunnels, and bridges, dam and reservoir linings and pipe coatings.

The question of whether roads paved with asphalt are a source of polycyclic aromatic hydrocarbons, and thus pose a potential health threat, has not been resolved. According to studies by Neukomm et al. (1975) and Just et al. (1971) there were no discernible differences in the concentration of PAH isolated from air and dust near roads paved with asphalt and roads paved with concrete. Neither study specified the exact composition of the "asphalt" highway. Waibel (1976) concluded that "bitumen" highways (13% coal tar pitch and 87% asphalt) are a significant source of benzo(a)pyrene. Contrasting a concrete and a bitumen highway of similiar traffic flow, Waibel (1976) found that dust generated from the bitumen pavement had over three times the BaP concentration (15 mg per one meter length of two lane road in winter; 10 mg in summer) of dust generated from the concrete. The majority of BaP was associated with particles between 15 and 30 micrometers in diameter.

5. Weathering and microbial degradation

Many of the major uses of asphalt are based on its permanence and persistence under conditions of prolonged exposure of large surface areas to the environment. Paving and roofing materials are constantly exposed to heat, light, water, wind and atmospheric oxidants. Road-building material are subject, in addition, to mechanical stress and abrasion by vehicular traffic and to the leaching effects of ice control chemicals. Waterproofing compounds and weatherproofing sealants may be constantly exposed to fresh or saline water.

Transformation of the physical structure of asphalt by heat, light, intermittent freezing, traffic stress, and erosion exposes additional surface area to the effects of weathering. Under these conditions, asphalt may be broken into particles small enough to be transported by wind and water. Weathering products of interest because of potential health effects include polynuclear aromatic hydrocarbons - including heterocyclic compounds as well as PAH - and trace metals. The contribuition of asphalt to the environmental load of polynuclear hydrocarbons and metals has not been examined.

Weathering

In paving materials, the primary cause of surface hardening seems to be volatilization or polymerization of the asphalt binder. In roofing asphalts, mechanical stress due to thermal shock results in surface cracks that signal failure; sunlight may catalyze the polymerization that is responsible for brittleness and subsequent cracking (Wright, 1965; Berry, 1960).

Oxidation, a primary weathering process that affects asphalt, results in the loss of water, carbon dioxide and volatile organic compounds. The asphaltene content of asphalts increases after oxidation, probably due to oxidation of oils. Formation and subsequent loss of water-soluble and volatile compounds result in weight reduction of the asphalt. The hardening following oxidation may be due to the conversion of resins to asphaltenes and oils to resins (Wright, 1965).

Although exposure of asphalt to oxidants other than O_2 accelerates aging, it is difficult to ascertain the impact of such prevalent air pollutants as nitrogen oxides, peroxides, sulfur oxides and ozone on the aging or degradation of asphalt (Wright, 1965). The use of antioxidants to retard asphalt aging has been proposed. Additives that decompose peroxides extend durability and retard asphalt weight loss (Wright, 1965).

Tests in which paving asphalts were exposed to heat in the absence of light, the presence of ultraviolet and the presence of infrared, suggest that light may have a substantial effect on asphalt performance. Under ultraviolet light, large decreases in penetration and increases in softening point occurred. The infrared exposure produced changes intermediate between the conditions of no light and of ultraviolet light (Vallerga et al., 1957).

Traxler and Scrivener (1971) implicated trace metals as catalysts in the hardening of asphalt observed after exposure to sunlight.

Exposure of asphalt to water accelerates aging of asphalt materials, probably due to the loss of water-soluble compounds, with subsequent exposure of a fresh surface to the elements. It has also been observed that asphalt degradation is hastened by increased humidity (Wright, 1965). Pure asphalt has a limited solubility in water, in the range of 0.001 to 0.01 percent; commercial asphalts, however, vary in their water absorption capacity depending on the presence of water-soluble salts or absorbing fillers such as gypsum, the use of catalysts in air-blowing, and the origin and hardness of the asphalt itself.

Although roads are subjected to mechanical stress, failure of the asphalt is due to increasing brittleness caused by volatilization and oxidation followed by polymerization. Failure of roofs is caused to a great extent by mechanical stress: during weathering, the asphaltene fraction increases at the expense of the oils and resins, resulting in insufficient oil to sustain the plastic structure of the asphaltenes. Severe cracking occurs, hastened by thermal shock and ultraviolet light (Wright, 1965).

Microbial degradation

All bitumens are potentially susceptible to biological degradation to some degree. Most bitumens, in fact, whether manufactured or naturally occurring, are attacked to some extent by a variety of microorganisms. It is difficult to ascertain the degree of damage to manufactured products or the extent of decomposition of native deposits, as well as the number and diversity of organisms capable of hydrocarbon utilization. A partial list of bitumen utilizers includes *Thiobacillus denitrificans*, *Mucor* spp, *Pseudomonas* spp, *Micrococcus* spp, *Bacillus* spp, *Alcaligenes* spp, *Mycobacterium* spp, *Chromobacter* spp, and *Flavobacterium* spp (Traxler, 1964).

Asphaltic components of crude oil can be assimilated by microorganisms under aerobic and anaerobic conditions, yielding, for example, hydrogen sulfide and asphaltenes (Atlas and Bartha, 1973). The effect of bacteria on asphalt viscosity has ben studied by Traxler *et al.* (1964). Brunnock *et al.* (1968) have reported tht residual oils, after degradation, have higher viscosities and increased sphaltene content, but unchanged paraffin profile and content of vanadium andnickel. The increase in asphaltenes as a result of microbial degradation o crude oil has also been reported by Walker *et al.* (1975a,b) and Jobson *etal.* (1972). It has been suggested that the observed increase in asphaltenes a mixture of polar, pentane insoluble compounds, may arise from the prodction of extracellular compounds such as carboxylic acids, esters and ketones.

Four species of fungi (*Cephalosporium acremonium*, *Penicillium* spp, *Cunninghamella elegans* and *Aspergillus versicolor*) were tested for their ability to utilise an phaltic base crude and a paraffinic base crude. After five days of growth in a medium containing basal salts plus crude oil, over 90 percent of the paraffinic crude had been assimilated. However, less than half that amount of asphaltic base crude had been utilized (Cerniglia and Perry, 1973).

Walker et al. (1975a,b) investigated the ability of an achlorophyllous alga, Prototheca zopfii, to degrade motor oil and a Louisiana crude. After thirty days, ten percent of the motor oil and forty percent of the crude oil had been degraded. The asphaltene and resin content of the motor oil increased, whereas these fractions decreased in the crude oil.

As a result of weathering and biological degradation, asphalt may release metals, organometallic complexes, polycyclic and heterocyclic hydrocarbons to the soil, air or water. The potential impact of metals such as vanadium, nickel and cadmium on the environment and on health has been reviewed by Berry and Wallace (1974), Braunstein et al. (1976), the National Research Council (1974, 1975), and the International Agency for Research on Cancer (1976). The formation, degradation, and bioaccumulation of PAH and their potential environmental impact have been reviewed by Braunstein et al. (1976), Andelman and Suess (1970), Andelman and Snodgrass (1974), Borneff (1975), National Research Council (1972), ZoBell (1971) and Radding et al. (1976). The limited information available on heterocyclic compounds has been reviewed by the International Agency for Research on Cancer (1973).

III. ENVIRONMENTAL EXPOSURE FACTORS: COAL TAR PITCH

A. Production and Consumption

1. Quantity produced

All of the coal tar commercially available in the United States is the residue of by-product coke oven tar distillation. Coke plants are classified as furnace plants (owned by iron and steel companies to produce blast furnace coke for their own use) and merchant plants (associated with chemical companies or gas utilities producing blast furnace or foundry coke for sale on the open market). In 1974, the 48 furnace plants accounted for 92 percent of the coke oven production and the 14 merchant plants for 8 percent (U.S. Bureau of Mines, 1975) (Table III-1).

2. Market trends

The absolute quantity of pitch available to process depends on the amount of coal tar produced, which, in turn, depends on the type and amount of coal carbonized for metallurgical coke production (Figures III-1,2). However, the amount of tar produced will always be roughly proportional to the metallurgical coke requirement (Mutschler, 1975). In 1974, all coke ovens produced tar varying between 6 and 9 gallons per ton of coal carbonized. Plants in West Virginia, Colorado, California and Utah used large percentages of high-volatile coals, and thus had higher yields of tar per amount of coal coked (U.S. Bureau of Mines, 1975).

Generally the amount of tar available for processing is limited first by the need for tar-pitch liquid fuels in steel-melting and blast furnaces (McGannon, 1971). In 1974, for example, coke plant operators

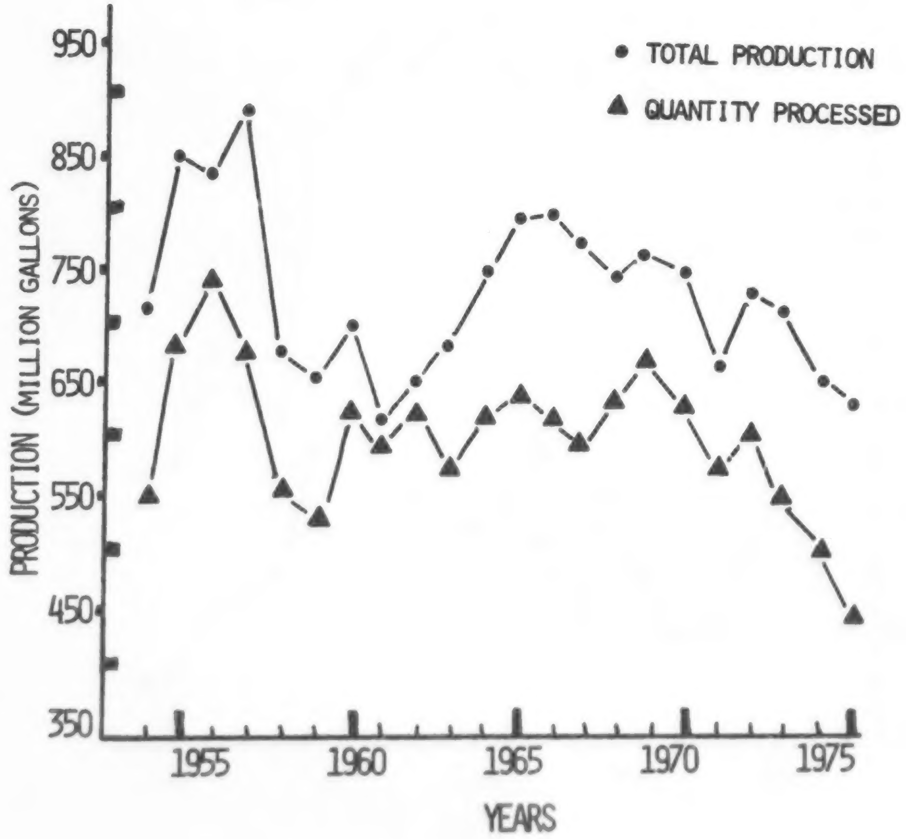
TABLE III-1
CRUDE TAR PRODUCTION AND PROCESSING: PITCH PRODUCTION 1954-1975

Year	Tar produced million gallons	Tar processed million gallons	Pitch* produced thousand tons
1954	716	556	1638
1955	853	679	2062
1956	833	734	2068
1957	873	674	1907
1958	669	555	1590
1959	654	534	1528
1960	688	616	1905
1961	633	604	2045
1962	650	610	1879
1963	672	573	1788
1964	763	602	1877
1965	803	616	2004
1966	802	605	1935
1967	780	595	1875
1968	761	644	1933
1969	769	667	1870
1970	761	658	1758
1971	679	572	1312
1972	747	593	1368
1973	732	554	1386
1974	677	503	1240
1975	646	450	1227

* Includes soft, medium and hard pitch, pitch of tar coke and pitch emulsion. Does not necessarily include road tar or other special tar categories.

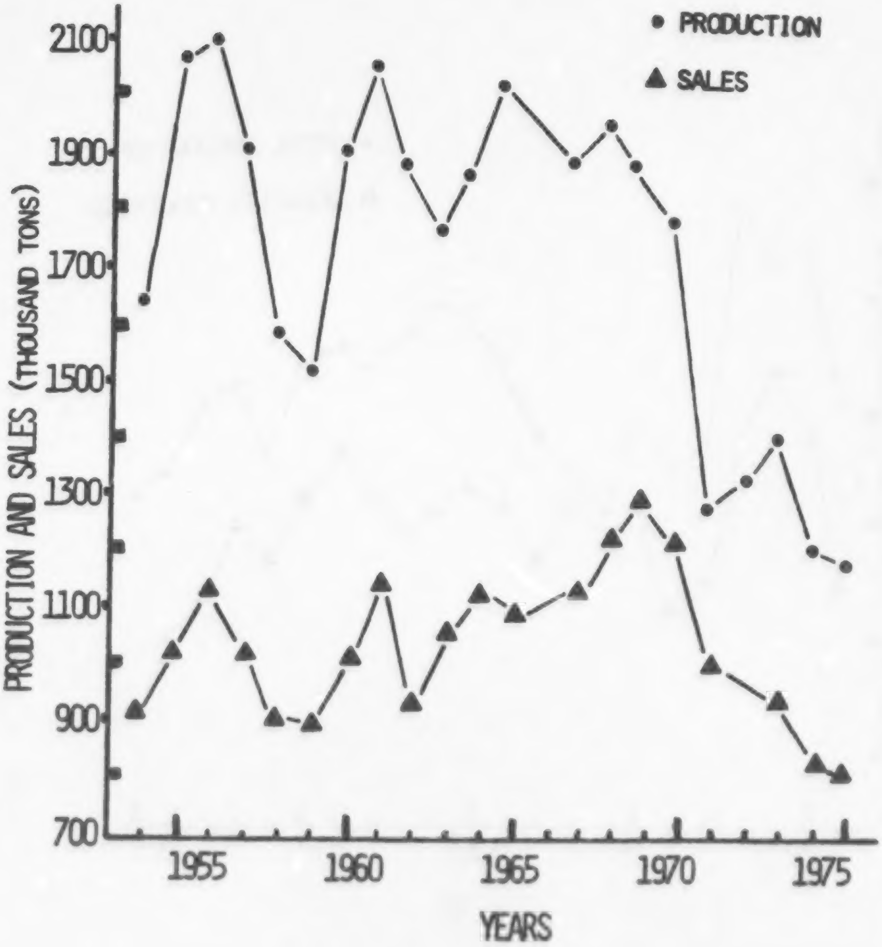
Source: U.S. International Trade Commission, 1954-1976

FIGURE III-1.
CRUDE COAL TAR PRODUCED AND PROCESSED
IN BY-PRODUCT COKE OVENS



Source: U.S. International Trade Commission, 1954-1976

FIGURE III-2. ANNUAL PITCH PRODUCTION AND SALES 1954-1975



Source: U.S. International Trade Commission, 1954-1976

consumed 55 percent of the coal tar produced; 50 percent of this was processed by the operators and 49 percent consumed directly as fuel. Thus, in 1974, 27 percent of the total tar from coking operations was consumed directly as fuel. In the past ten years, this percentage has generally varied between 12 and 27 percent (U.S. International Trade Commission, 1966 - 1976).

Until recently, the coal tar pitch market was dominated by the use of pitch as a fuel. The importance of pitch as a binder in carbon and graphite products has increased, however, with the largest single use of pitch being as a binder in carbon electrodes used in the manufacture of aluminum (Table III-2).

In the past three years, demand for metallurgical coke has averaged approximately 85 million tons annually (Coal Age, 1976). By 1985, assuming no major changes in iron reduction technology, annual metallurgical coke demand should reach 109.4 million tons (Mutschler, 1975).

Formcoke briquetting (no description found in the literature) has been proposed as an alternative to coke oven production of metallurgical coke. Currently, a formcoke pilot plant is being tested at Sparrow Point, Maryland, by a consortium of four steel companies and one coal company. At Inland Steel's Indiana Harbor Works, East Chicago, Indiana blast furnace operation and iron quality were normal in test runs using up to 50 percent formcoke. (U.S. Bureau of Mines, 1975). If formcoking is successfully implemented by 1985, demand for metallurgical coke could be as low as 67 million tons annually (Mutschler, 1975).

Potential sources of pitch are coal liquefaction and gasification, of which a number of bench scale models and pilot plants are now being tested. Each different process has different effluent problems: for example, the Hygas process yields negligible quantities of tar, but high concentrations

TABLE III-2. CONSUMPTION OF COAL TAR PITCH BY MARKET (THOUSAND TONS)

Use	Average 1950-52	1960	1964	1977*
Fuel	822	925	912	200
Binder for carbon products	200	220	490	720
Roofing	280	na	130	80
Fiber pipe	65	95	95	na
Coatings	130	90	90	na
Misc. (total)	130	150	160	150
Refractory pitch	na	na	na	6
Target pitch	10	10	10	10
Foundry sands	na	na	25	na

na = not available

*Projected figures

Source: Cohrssen, 1977

of phenol. On the other hand, the Synthane process yields negligible phenol concentrations, but large amounts of tar. The quantity of a "by-product" such as phenol, oil or tar within one system can vary as much as 100-fold depending on process variables (Massey, 1977).

3. Market prices

From 1969 until 1973, the price of crude coal tar increased from $0.10 per gallon to $0.12 per gallon. In 1974 and 1975, coal tar was worth an average of $0.33 per gallon (U.S. International Trade Commission, 1976). From 1964 to 1974, the value of pitch increased from $39 per ton to $95 per ton (Table III-3). The current average price for soft, medium and hard pitch exceeds $102 per ton and is expected to continue increasing (U.S. International Trade Commission, 1954-1977).

4. Producers and distributors

In 1975, five of sixty-two coke oven plants listed pitch as a by-product in information given to the U.S. Bureau of Mines, Division of Fuels (1976b). These plants are:

U.S. Steel Corp., Fairfield, Alabama
Gary, Indiana
Clairton, Pennsylvania

Bethlehem Steel Corp., Johnstown, Pennsylvania

Wheeling-Pittsburgh Steel Corp., East Steubenville, West Virginia

This information implies, perhaps not accurately, that all other pitch was derived from tar distillation, rather than by-product coking, at facilities other than coke ovens.

The following companies may be considered producers and/or distributors of coal tar pitch (Oil, Paint and Drug Chemical Buyers Guide 1975-76; U.S. International Trade Commission, 1976):

TABLE III-3. PITCH SALES AND VALUE

Year	Sales (thousand tons)	Value (dollars)	Unit Value[1] (dollars/ton)
1964	1119	43,700	39
1965	1081	38,400	36
1966	1167	43,100	37
1967	1128	40,900	36
1968	1219	40,900	34
1969	1311	41,500	32
1970	1292	46,400	36
1971	1033	48,200	47
1972	1009	48,600	48
1973	1001	50,800	51
1974	882	83,600	95
1975	888	90,300	102

[1] This value represents an average of unit values for soft, medium and hard pitch.

Source: U.S. International Trade Commission, 1964-1976

Allied Asphalt and Mineral Corp.
Allied Chemical Corp., Semet-Solvay Div.
Coopers Creek Chemical Corp.
Crowley Tar Products, Inc.
Donner-Hanna Coke Corp.
Bethlehem Steel Corp., Interlake, Inc.)
Husky Industries
Jennison-Wright Corp.
Koppers Co., Inc. Organic Materials Div.
Ore and Ferro Corp.
Reilly Tar and Chemical Corp.
Samuel Cabot, Inc.
USS Chemicals, Div. of US Steel Corp.
Witco Chemical Corp., Pioneer Div.
Ziegler Chemical and Mineral Corp.

5. Production process

Pitch is the residue from fractional distillation of the tar that volatilizes during the destructive distillation of coal. There are 62 coke oven batteries operating in the United States, two-thirds of which are more than twenty years old. Ninety-two percent of the coke produced is used as a reducing agent in blast furnaces; eight percent is used as foundry coke (U.S. Department of Labor, 1975).

Information in the following section on the basic method of pitch production was derived from McNeil (1966a,b; 1969), U.S. Department of Labor (1975), and Lauer (1974).

Coal is coked at high temperatures (above 1100°C) in the absence of air for an average of 18 hours. Softening of the coal begins above 350°C; fluidity increases as the temperature increases. Between 400° and 500°C, most of the volatile tar and gases, which represent 20 to 35 weight-percent of the initial coal charged, are evolved, then collected for by-product recovery. Above 550°C the residue solidifies, although some gas is still evolved. By 900°C, the solid residue is coked; continuing the process at higher temperatures results in a coke of greater purity.

The tarry volatiles and gases are removed through refractory-lined standpipes to a collecting main where their temperature is reduced from 600° or 700°C to 100°C by spraying with a dilute ammonia liquor. The gases, tar and liquor are then separated.

Primary distillation of tar involves "topping" (stripping off fractions boiling below 300°C), leaving a refined (base) tar residue. There is no strict delineation between the base tar and soft pitch, although the base tar is usually defined as having a softening point of less than 50°C. Soft pitch has a softening point (ring and ball) of 50° to 75°C, medium pitch a softening point of 75° to 85°C, and hard pitch a softening point of 85° to 120°C. Although pitch can be cut back with lower boiling coal tar fractions to yield softer grades, it is ordinarily the extent of distillation that determines the pitch hardness. Topped tar and soft pitch include quantities of the creosote fraction, which may contain 12 to 14 percent phenanthrene and 2 to 4 percent acenaphthene, fluorene, diphenylene oxide, anthracene and carbazole, as well as naphthalene and phenolic compounds.

Although there are many variations in process design for tar distillation, most are highly automated processes. The essential features include a refractory brick lined tube-still furnace through which the tar flows, flash chambers in which water and volatiles are separated from the crude tar, and one or many bubble-cap fractionating columns in which tar vapors are separated by boiling range. Most tar distilleries use multiple flash chambers to separate out the pitch before fractionating the tar. Because tars are thermally unstable, overheating, the most dire consequence of which is coke formation in the apparatus, is avoided during distillation.

B. Uses

1. Major uses

Information in the following two sections was derived from Liggett (1964), Lauer (1974), Shuler and Bierbaum (1974), and Encyclopaedia Britannica (1969).

Aside from consumption as a fuel in open-hearth furnaces, the major usage of pitch is as a binder and an impregnant in baked and graphitized carbon products. Pitch, because of its high specific gravity, high carbon content and plasticity at the temperatures used in graphite manufacture, is utilized as a binder for petroleum coke (derived from delayed coking of heavy residual oils or asphalt) or for carbon black, natural graphite, gilsonite coke and anthracite coal. In the production of commercial carbon products the pitch binder and petroleum coke (or other) filler are subjected to temperatures of 950° to 1100°C; the production of graphite requires temperatures up to 3000°C. Following baking and impregnation with hot pitch, the pitch-coke mixture may be used directly (e.g. carbon anodes in aluminum production), or graphitized before use (e.g. specialty products, resistors in electrolytic furnaces and foundry mold facings).

Of the pitch used in baked and graphitized products, the greatest quantity is consumed in various electrode applications. Direct-heating electrolytic furnaces for aluminum, lithium, potassium, sodium, calcium and magnesium production commonly use prebaked carbon anodes. In the case of aluminum production, 540 pounds of baked carbon anode delivers approximately 130,000 amperes of direct current to a submerged bath of alumina, molten cryolite and aluminum fluoride. The aluminum collects at the "cathode" formed by the carbon refractory lined pot bottom, while oxygen collects at the anodes which are consumed during the process. About 50 pounds of carbon anode are required for 100 pounds of aluminum produced.

Carbon electrodes are also used in the following processes: electric arc furnace melting and refining of ferrous metals; submerged arc electric furnace production of phosphorus, ferroalloys, and calcium carbide; and diaphragm-type and mercury-cathode-type caustic chlorine cells.

Although prebaked carbon electrodes are most commonly employed, the applications of the Soderberg (self-burning) electrode are increasing. This electrode is extruded as a soft paste of calcined filler (petroleum coke) and pitch binder (25 to 35 weight-percent) into an electrolytic bath; the electrode is coked at 950°C, consumed and continuously replaced during the process of use.

Uses of pitch that depend primarily on its heat resistance qualities are taking over an increasing portion of the baked carbon market. Carbon refractories are a relatively recent development in the metal and glass industries. The addition of pitch to a firebrick formula results in brick that can withstand the physical and chemical stresses encountered as part of a furnace lining that must tolerate temperatures up to 2000°C as well as the corrosive action of molten metal or glass slag.

Pitch-bonded bricks are usually composed of sintered magnesite or dolomite and coal tar pitch, the pitch inhibiting hydration of the minerals. The mixture of sintered mineral filler and binder is pressed into shape at 130°C. The pitch is coked as the bricks are fired. Pitch is also used to impregnate super-duty fire clay and alumina brick. The heated bricks are pressure impregnated at 200°C and contain six precent by volume pitch when finished. The bricks are not fired to carbonize the pitch.

Refractory bricks may be used in the basic oxygen steel furnace, blast furnace, pots used in aluminum and alkali metal manufacture, electric reduction furnaces in ferroalloy manufacture, and in foundry cupolas.

Specialty carbon products requiring the use of graphite include dies for high-temperature metal molding, graphite seals, bushings, carbon brushes, pencil "lead", woven graphite felt for high temperature insulation, arc welding materials, foundry castings for highly reactive metals (titanium, molybdenum, zirconium), and nuclear reactor moderators.

Carbon anodes used in aluminum production are often manufactured by the primary aluminum producer. Other manufacturers of carbon and graphite products include Airco-Speer Carbon-Graphite, Carborundum Co., Great Lakes Carbon, Collier Carbon and Chemical, and Union Carbide.

2. Minor Uses

In 1969, 55 million gallons of tar, including pitch and tar used by homeowners for blacktopping driveways, were used in the United States for road building (Lauer, 1974).

Roofs covered with pitch are almost entirely confined to large, low slope commercial warehouses, factories or large buildings. Roofing uses, including "tar" saturated felts, pitch cements and cutbacks, were expected to require the use of 80 thousand tons of pitch (softening points of 50° to 60°C) in 1977 (Table III-2).

About 10 thousand tons are used annually to manufacture clay pigeons used in trapshooting. "Target pitch" has a softening point of 125°C or higher and is mixed with pulverized minerals like limestone, then molded into the traditional saucer-shaped target. The pitch imparts brittleness which enhances the shattering (Lauer, 1974).

The use of pitch in waterproof coatings has declined, largely because of competition from asphalt and synthetic materials. Some specification coatings are produced, but information and estimates about them are unavailable (Lauer, 1974).

Coal tar has been widely used in a variety of topical medications such as dandruff and fungicidal shampoos, acne remedies and ointments for psoriasis and eczema.

C. Environmental Contamination Potential

1. Emissions from production

a. Coke ovens and tar distilleries

A number of studies have been directed at determining the magnitude of hazard that coke ovens present, both to the worker and to the general public. Levels of PAH in airborne emissions at one such steel and coke operation are presented in Table III-4. Almost no work, however, has been done to determine whether tar distillation facilities, either part of a by-product recovery system or independently operated, contribute polynuclear aromatic hydrocarbons or metals to the environment.

Masek (1972) collected suspended dust and air samples in three Czechoslovakian coal tar distilleries, particularly focussing on areas where the tar and pitch were pumped and storage vessels emptied and filled. Benzo(a)pyrene levels in the dust ranged from 121 to 2544 $\mu g/g$, primarily associated with dust of less than five micrometers diameter. Levels of BaP in the air ranged from 0.30 to 8.49 $\mu g/m^3$. Most PAH emissions in modern tar distilleries are a result of leakage around seals (Masek, 1972; von Lehmden *et al.*, 1965).

b. Graphite manufacture

The production of any baked or graphitic carbon product begins with certain basic steps: calcined filler is pulverized, cleaned and sized, then mixed at 140 to 175°C with pulverized or heated liquid pitch, which constitutes 15 to 30 weight-percent. Once the petroleum coke (filler) and pitch mixture has been molded or extruded (at about 100°C and 400 to 8000 psi) it is baked, perhaps as long as four weeks, in a gas-fired furnace at 950° to 1100°C, then

TABLE III-4. LEVELS OF AIRBORNE PAH IN EMISSIONS ASSOCIATED WITH AN INTEGRATED STEEL AND COKE OPERATION

PAH	Concentration (μg/g suspended particle)
Benzo(a)pyrene	89
Benzo(e)pyrene	43
Benzo(ghi)perylene	77
Coronene	4.1
Anthracene	29
Fluoranthene	33
Pyrene	75
Perylene	10

Source: von Lehmden _et_ _al_., 1965

slowly cooled. At the end of the baking period, 10 to 15 percent of the green (uncoked) body weight will have been lost; 30 to 40 percent of the binder will have volatilized, as emissions which may or may not be adequately controlled, and the remainder coked. After cooling, the baked carbon may be impregnated with hot pitch and subjected to temperatures up to 3000°C. It is important to note that the pitch component is not present in the final graphitic product (Oil, Chemical, and Atomic Workers International Union, 1977).

Large amounts of dust are produced during the grinding, mixing and handling of the petroleum coke and the pitch. Coal tar pitch volatiles may be present during baking and impregnation. Pitch may contain vanadium, iron, boron, lead, and other metals, which are a potential hazard.

No work has been found that examines emissions from carbon baking and graphitizing; however, a study by Griest et al. (1977) examines fugitive emissions associated with a bench scale graphite production operation. The grinding of pitch-coated coke resulted in high BaP concentrations, 0.23 to 0.63 mg/m^3 air. In measurements taken to determine ambient levels of BaP not associated with any particular operation, the BaP concentration reached a peak of 0.72 mg/m^3. The study does not necessarily reflect working conditions or the type and quantity of emissions escaping to the atmosphere.

Electrodes used by primary aluminum producers are often manufactured in-house. Several suggestions for minimizing air pollution from carbon anode manufacture include the use of air pollution abatement equipment - scrubbers, multicyclones, baghouses and fume incinerators - and the use of carbon anodes prebaked at 1100°C rather than self-burning (Soderberg) electrodes to eliminate most of the volatiles in the pot room (Donaldson et al., 1972; Larsen, 1973; Shuler, 1973).

c. Other production processes

Pitch can be modified in much the same ways as asphalt. Air blowing pitch at 220° to 360°C will increase the binder resin content. Subjecting pitch to pressures from 50 to 500 psi at 370° to 488° C for several hours produces a harder pitch. (Hoiberg, 1966). No information on the practices of air blowing or thermal treating was found for pitch.

Bolotova et al. (1967) measured BaP emissions in and near a plant making pitch-saturated roofing materials. The pitch was maintained at 120°C. The BaP level in the plant was 0.001203 mg/m^3; at a distance of 100 meters from the plant it was 0.000129 mg/m^3 ; at 500 meters it was 0.000047 mg/m^3.

Sawicki (1967) reported the BaP level near a sidewalk tarring operation as 0.078 mg/m^3.

Samples of fresh fumes obtained under experimental conditons from coal tar pitch maintained at 200°C consisted largely of phenanthrene and anthracene (Table III-5) (Hittle and Stukel, 1976). Low fume or no-burn pitch (Koppers Co.) is available for roofing operations and its use should be encouraged (Hervin and Emmett, 1976b; Hittle and Stukel, 1976).

Air polluted by coal tar pitch fumes is characterized by high pyrene/BaP, BeP/benzo(ghi)perylene, and BaP/coronene ratios (Sawicki et al., 1962). Heterocyclic compounds such as acridine, carbazole and their derivatives may also be present in pitch fumes (White, 1975; Sawicki et al., 1965).

2. Contamination potential from storage, transport and disposal

Because pitch is often used in liquid form, it is economical to store and ship it at elevated temperatures as a liquid (Smith et al., 1966). Solid pitch is handled as flakes or rods (McNeil, 1969). No information on contamination from pitch storage or transport was found.

TABLE III-5. COMPOSITION OF FRESH FUMES FROM ROOFING PITCH

PAH identified	Weight Percent
Phenanthrene/anthracene	36.4
Fluoranthene	11.8
Carbazole	9.6
Fluorene	9.1
Pyrene	8.5
Naphthalene, its methylated derivatives, and xanthene	24.6

Source: Hittle and Stukel, 1976

No information on disposal of pitch was encountered; it is unlikely that significant quantities are simply thrown away since pitch can be used as a fuel.

3. Contamination potential from use

Pitch and tar-pitch mixtures are important fuels for the open hearth furnace (McGannon, 1971). The background levels of coal tar pitch volatiles in steel and coke operations make it difficult to ascribe blame to any single substance or operation. No study addressing itself to pollution by pitch as a fuel was found.

The largest market for pitch is as an electrode binder and impregnant, yet little attention has been paid to this potential source of carcinogenic polycyclic and heterocyclic compounds or metals. In theory, graphite electrodes lose the volatile components during baking and graphitization and are no longer a source of PAH during use. In contrast, carbon electrodes not only lose volatiles throughout the entire baking process (Gromiec, 1975), but they may also be a source of PAH during use. Soderberg (self-burning) electrodes are a significant source of pitch volatiles (Shuler and Bierbaum, 1974; Larsen, 1973; Konstantinov and Kuzminyuk, 1971).

Electric arc furnaces may be lined with carbon refractories; carbon electrodes may be used in them as well. Tanimura (1968) measured BaP levels of 0.286 mg/g suspended particulate near an electric steel furnace; no source of the BaP was suggested.

The contribution of pitch to foundry pollution is not documented. A review by Bates and Scheel (1974) indicates that much work on foundry pollution, whether or not caused by pitch, needs to be done.

Clay pigeons have been implicated as the source of pitch which has caused poisoning in livestock up to 35 years after an area was used for trapshooting (Kernkamp, 1964). Usually poisonings occur one or two years after the initial deposition of target pitch.

In addition to being a source of PAH, pitch may be a source of metals. Little work has actually been done on the trace metal content of pitch and its volatiles except as metals affect engineering performance. Levels of trace metals in pitch volatiles at a coke oven battery were determined by Schulte et al. (1975). Zinc constituted over half the metal concentration; copper and manganese were of intermediate concentration; traces of nickel and chromium were found. Also present in pitch are vanadium, iron, and boron (Liggett, 1964).

4. Weathering

There has been much less work done on the weathering of pitch than of asphalt, probably becauses the uses in which pitch is exposed to the environment are in its smaller markets: paving, roofing and coatings. The most significant factors in pitch weathering are evaporation of the more volatile tar fractions and oxidation. Pitch is highly water resistant and shows little response to ultraviolet light (Phelan and Rhodes, 1966).

Asphalt and occasionally coal tar pitch are used as soil stabilizers. A study by Perov (1969) on the migration of heavy coal tar fractions suggests that the use of pitch should be avoided for soil applications. Pitch can contain anthracene oil, phenolic and cresolic compounds. The anthracene fraction migrates slowly and tends to be retained at shallow depths for prolonged periods. The phenolic and cresolic compounds pass through the soil column quickly and accumulate in deeper layers. Decomposition of these heavy coal tar fractions, which are present in appreciable concentration in pitch used for road work and bank stabilization, proceeds slowly. Perov (1969) concludes that elution of water-soluble compounds from heavy coal tar fractions is a potential threat to groundwater supplies.

As a result of weathering and biological degradation, pitch may release metals, organometallic complexes, polycyclic and heterocyclic hydrocarbons to the soil, air or water. The reviews on metals and PAH mentioned in Section II. C.5. (asphalt) can be useful in evaluating the potential hazard of pitch in the environment. Considering the variety and potential carcinogenicity of compounds which may be made available from weathered pitch or from pitch fumes, much work needs to be done on the subject of bitumen degradation.

IV. ANALYTICAL METHODS

A number of analytical techniques in various combinations have been developed for the identification and determination of some of the components of complex bituminous mixtures such as asphalt and pitch.

Complex mixtures derived from fossil fuels, such as coal tar pitch and asphalt, contain many chemicals of biological significance. There has been a great need to identify these compounds, especially the polynuclear aromatic hydrocarbons (PAH) and aliphatics. Among these are carcinogens, cocarcinogens and inhibitors. Such components may be distributed throughout products derived from these complex mixtures or may be disseminated into air, water and soil.

A. Sampling

High volume air samplers are used to collect atmospheric samples by drawing air through filters at varying velocities. Glass fiber filters without binders, which are relatively inexpensive, remove nearly all particles greater than 0.3 microns (Hoffman and Wynder, 1968; Kukreja and Bove, 1976). Richards _et al_. (1967) compared glass fiber filters, cellulose acetate membranes, cellulose filters, and cellulose thimbles with silver membrane filters. The study included determination of weight stability due to humidity changes and extraction procedures. The conclusion was that silver membrane filters were most suitable for use in the evaluation of atmospheric concentrations of coal tar pitch volatiles. Silver membrane filters, also used in personal air samplers (Seim _et al_., 1974; Richards _et al_., 1967; Masek, 1970) have a pore size of about 0.8 microns and show very little weight loss after benzene extraction, but tend to load up rapidly with a resultant decrease in flow. When compared to glass fiber filters, silver membrane filters have a high tare weight and are relatively expensive.

Millipore filters have been used for collecting metals in coke oven emissions (White, 1975). Several types of combination filters have been used in personal samplers (U.S. National Institute for Occupational Safety and Health, 1977a,b). Since low molecular weight PAH pass through various combinations of silver and glass filters (Schulte et al., 1974, 1975; Seim et al., 1974, 1975a,b), cellulose backup pads have been used with glass fiber filters without organic binders followed by a silver membrane filter. Use and analysis of such a backup pad has been advised in order to detect all material passing through the filters. However, in some instances a trap consisting of charcoal or resin material is also necessary to absorb the more volatile PAH passing through the mechanical filters (Jones, 1977). When sampling for particulate matter, asphalt fumes and coal tar pitch volatiles are considered PPOM (particulate polycyclic organic matter), for which a glass fiber filter without a silver membrane backup is presently considered to be adequate (U.S. National Institute for Occupational Safety and Health, 1977a,b).

More than fifty different types of instruments have been used to sample particulates (Roach, 1973). The mass concentration or the number concentration of particles in a volume of gas can be determined with the use of appropriate samplers. Instruments used to measure mass concentration of a particulate can be equipped with preselectors, such as elutriators or cyclones, to separate coarse nonrespirable particulates before collection. Due to the adhesive property of asphalt fumes a preselector can induce error by trapping respirable particulates, while collection without a preselector can induce error by including in the calculated mass of asphalt fumes the amount of total particulate in the nonrespirable size range (U.S. National Institute for Occupational Safety and Health, 1977a).

Sizing of particles has been performed on emissions. Five- and seven-stage high volume samplers using combinations of glass slides and glass fiber filters have been used to determine the amount of respirable particles (Kertesz-Saringer et al., 1971; Natusch and Wallace, 1974; Hittle and Stukel, 1976). White (1975) has sized particles on low volume samplers using aluminum foil.

Other sampling devices have been used less frequently: a high volume sampler collecting particulate on paper filters (Tanimura, 1968), an electrostatic precipitator to collect samples of tar vapors (Bonnet, 1962; Hoffman and Wynder, 1968), a greased-plate technique to sample particulate concentrations in a quench tower during quenching of hot coke (Fullerton, 1967), cascade impactor and thermal precipitation to collect samples in a retort house (Lawther et al., 1965), and bubbling air through solvents to collect samples at a coke plant (Bondarava, 1963).

There are major problems with the sampling methods and filters. Materials to be sampled may be incompletely collected on the filters, as indicated by their presence on backup pads or charcoal tubes. In addition to differences in sampling efficiency for various compound types, the entire range of respirable particulates (submicron to 10 microns) may not be collected on the filters used. Heat, increased air velocity, sunlight, and ultraviolet have been found to decompose or volatilize some PAH, resulting in yields as low as one tenth of the actual value (Commins and Lawther, 1958; Rondia, 1965; Thomas et al., 1968; Katz and Monkman, 1964). Collection of the samples at normal environmental temperatures (20°C) and storage of the samples in a cool, dark location would minimize the volatilization of PAH (Rondia, 1965) and the decomposition of even the most unstable PAH (Hoffman and Wynder, 1968).

B. Methods of Sample Analysis

Some preliminary separations of asphalt, coal tar pitch, asphalt fumes, or coal tar pitch volatiles into their components are necessary prior to the use of chromatographic separations. These initial separations usually involve solvent extractions and/or precipitations, fractional distillations and gravity fed adsorption chromatography. Additional adsorption chromatography, as described in Section B.1.d., can then be used to separate the components further into fractions that can be analyzed by sophisticated detection methods. The chromatography can be used in conjunction with or prior to the use of analytical tools for quantitation, as described in Section B.2.

1. Separation Schemes

a. Solvent Extraction and/or Precipitation

A number of extractions (liquid-liquid or solid-liquid) and precipitations are used (as described in Chapter I) in fractionating asphalt and coal tar pitch into more manageable components containing PAH and metals. Similar extraction methods are used for tar, petroleum and crude air samples. Some of these methods have been developed for concentrating and isolating metals and organic compounds found in crude air samples (Hoffmann and Wynder, 1968; Hueper *et al.*, 1962), cigarette smoke condensate, (Swain *et al.*, 1969; Severson *et al.*, 1976; Snook *et al.*, 1975; Finelli *et al.*, 1972), white petroleum products (Popl *et al.*, 1975), carbon black (Gold, 1975), heavy end distillates (Altgelt and Gouw, 1975), carbon paste plants (Bjørseth and Lunde, 1977), marine organisms (Warner, 1976), and coal tar and coal tar pitch (White, 1975).

In the coal tar and coal tar pitch method of White (1975), based on the procedure of Swain *et al.*, (1969), about 100 grams of coal tar is dissolved in 500 ml of ether. The coal tar solution is extracted with ten percent aqueous sodium hydroxide to remove the tar acids, ten percent hydrochloric acid to extract the tar bases, and ten percent sulfuric acid to extract the aliphatic olefins. The remaining solution, combined with ether washings of these aqueous extracts, constitutes the neutral fraction of coal tar. The raw coal tar sample is thus separated into particulate matter (20%), neutral (60%), basic (3%), acidic (weak and strong) (3%), and water soluble (14%) fractions.

b. Solid-Liquid Extraction

Most particulate air samples (asphalt fumes or coal tar pitch volatiles) collected on filters use some type of Soxhlet (solid-liquid) extraction (Karasek et al., 1978). Soxhlet extraction glassware has been widely used for solid-liquid extraction since the samples can be washed with clean redistilled solvent and the extract collected and concentrated at the same time.

Soxhlet extractions with acetone have been used for more than 20 years in England to extract PAH (Waller, 1952). Benzene is a very good but potentially hazardous solvent which completely extracts PAH from particulates with diameters greater than 80 microns (Hoffman and Wynder, 1968). The extractions are carried out at temperatures below 80°C to prevent decomposition of BaP. A variety of other solvents such as pentane, cyclohexane, diethyl ether, methylene chloride, and ether:toluene:cyclohexane (1:2:1) have been tried with reasonably good recovery. The polar PAH, however, are not extracted quantitatively (Stanley et al., 1967; White, 1975).

With benzene, a large amount of background material is also extracted, complicating further analyses which involve isolation, identification and quantitation of compounds present in low concentrations. Cyclohexane is considered preferable to benzene since it will remove most of the PAH with less background material (Lijinsky et al., 1963).

The PAH extracted are subject to decomposition by UV radiation, and therefore the work is carried out under yellow light (Tanimura, 1968). Total particulates are measured as the difference in weight of the filter before and after sampling, following conditioning in a desiccator. The benzene solubles can be determined by weighing (1) the residue after evaporation to dryness of 5 ml of the extract, or (2) the filter before and after extraction. The weight is then related to the volume of air passing through the filter averaged over the time of collection.

A number of objections, however, have been raised by investigators concerning Soxhlet extractions (Seim et al., 1974, 1975b; Schulte et al., 1974, 1975; Golden and Sawicki, 1973). The extractions have been found to be unreliable and not reproducible. The extraction procedures are time consuming, decompose some of the pollutants, lack precision, do not collect all of the PAH, lose some of the volatiles, lose particulates during handling and extraction and do not correlate well with PAH content. Filter disintegration and change in water content between weighings cause further problems.

New gravimetric methods are being developed which involve ultrasonic extraction of the filter with benzene, carbon disulfide, or cyclohexane. After sonication for five to ten minutes, an aliquot of the extract is evaporated in a teflon weighing cup and weighed on an electro balance (Seim, 1975b; Golden and Sawicki, 1973). Modifications of these methods are being developed by various government agencies, such as the U.S. National Institute for Occupational Safety and Health (1977) and the Occupational Safety and Health Administration. Such methods avoid problems generated by the Soxhlet extractions.

Trace metal samples are collected on high volume glass fiber filters. The filters are wet ashed with ultra pure acids and the resulting ash is taken up in solution. The sample is then analyzed by analytical tools for various metals (Schulte et al., 1974, 1975; Fassel and Kniseley, 1974).

c. Distillation

Fractional distillation has been used for samples with wide boiling ranges (Sawicki et al., 1964). Phenols, nitrogen bases, PAH, paraffins, and anthracene in coal tar pitch have been separated by distillation (Charette and Bischofberger, 1961). Initial separations have also involved vacuum distillation (Altgelt and Gouw, 1975).

d. Chromatography

Chromatographic separations mainly concerned with organic compounds are usually performed after distillation and/or solvent extractions and precipitations. There are a wide range of chromatographic techniques, such as gas chromatography (GC), gel permeation, ion exchange, and paper and liquid adsorption, that have been discussed in detail in numerous reviews concerned with coal tar, coal tar pitch and coal tar pitch volatiles (Schulte et al., 1974, 1975: White, 1972, 1975), heavy end distillates (Altgelt and Gouw, 1975), and asphalt and asphalt fumes (Couper, 1977; Schweyer, 1975; Knotnerus, 1967). Less commonly used techniques are also discussed in these reviews.

Adsorption:

Liquid adsorption chromatography techniques include gravity fed column, thin layer, and high performance liquid or high pressure liquid (HPLC). The adsorbents that are used include florisil, silica, alumina, charcoal, magnesia and sephadex LH-20 (Altgelt and Gouw, 1975). Modified adsorbent materials consisting of high molecular weight polymers coated or bonded to the surface of chromatographic supports are now being applied more readily to HPLC work.

Alumina and silica gel are the most commonly used supports in gravity fed column chromatography. Solvents with necessary polarity from pentane to ethanol are used in succession or in combination to effect separation of mixtures into aliphatic, aromatic, and heterocyclic compounds. This type of chromatography has been applied to the separation of crude air samples (Hoffman and Wynder, 1968; Hueper et al., 1962), cigarette smoke condensate (Swain et al., 1969; Snook et al., 1975), white petroleum products (Popl et al., 1975), carbon black (Gold, 1975), coal liquefaction products (Goeckner and Griest, 1977), and aromatics(PAH in particular) from coal tar and coal tar pitch volatile extracts and fractions (Karr et al., 1964; Tanimura, 1968; Sawicki et al., 1962, 1965). Gravity fed column chromatography has also been used in the separation and characterization of total hydrocarbons from low temperature coal tars (Rizvi et al., 1971). However, this technique is slow and often requires arbitrary decisions to be made at the end of each cut due to variable retention volumes brought about by matrix effects. This separation method may require days or weeks.

Thin layer chromatography (TLC) is a simple, rapid, versatile and inexpensive method. However, for complex mixtures it is more time consuming and difficult than paper or column chromatography. Compounds are characterized by R_f values (distance traveled by compound/distance traveled by solvent), standards, and fluorescence colors (Sawicki and Sawicki, 1972). TLC is used in the separation of PAH from air samples (Lannoye and Greinke, 1974; Sawicki et al., 1970d,e) and of PAH and basic heterocyclic compounds, BaP, and phenols from coal tar pitch volatile extracts and fractions (Sawicki et al., 1964; Zoccolillo and Liberti, 1976; Seeboth, 1963; Stroemberg and Widmark, 1970; Pierce and Katz, 1975). Problems generally encountered with TLC are sample size, interferences, recoveries, reproducibilities, and compounds bound strongly to adsorbent (Sawicki et al., 1964, Sawicki and Sawicki, 1972).

A more recent method for the determination of PAH by channel TLC shows promise as a rapid reliable means of analyzing air samples and oils (Zoccolillo and Liberti, 1976).

The increasing use of high pressure liquid or high performance liquid chromatography (HPLC) (Hadden et al., 1971; Brown, 1973; Simpson, 1976) for separation and determination of PAH has led to (1) reduction in purification time, (2) optimization of fractional resolution, and (3) reproducibility of fraction collecting. Due to the availability of highly efficient micropacked analytical columns (for samples $\leq$ 3 mg) with various adsorbents, programmable solvent mixtures, and mass spectrometry detection methods, mixtures of aromatic compounds have been successfully separated and analyzed for PAH at room temperature in a matter of hours. The PAH in the samples can be collected without decomposition, already in solution for further analysis. In some instnces HPLC has eluted and resolved high molecular weight PAH (five to seven rings), such as benzo(e)pyrene from benzo(a)pyrene, in less than half the time required for the same separation on a packed column by gas chromatography at elevated temperatures (Thomas and Lao, 1977; Jones and Yang, 1975; DeStefano and Kirkland, 1975; Klimish, 1973a,b; Klimish and Fox, 1976; Soedigdo et al., 1975; McLafferty et al., 1975; Wheals et al., 1975; Goldstein, 1976; Hunt et al., 1977; Ives and Giuffrida, 1972). HPLC has been used in the analysis of heavy end petroleum distillates (Suatoni and Garber, 1976; Suatoni and Swab, 1975, 1976; Schmit et al., 1971; Jewell et al., 1972a,b; Hirsch et al., 1972; Vogh and Dooley, 1975), asphalt and asphalt fumes (Couper, 1977; Schweyer, 1975), crude air samples (Dong et al., 1976; Fox and Staley, 1976) and fossil fuels (Thomas and Lao, 1977), and to measure the solubility of PAH in aqueous systems (May et al., 1978).

Gas-Liquid (GC):

GC using packed or capillary columns is a rapid and versatile tool for analysis of low molecular weight compounds that can be volatilized without decomposition. It is a widely used separation technique in the analysis of heavy end petroleum distillates (McKay et al., 1976; Youssef et al., 1976; Altgelt and Gouw, 1975), asphalt and asphalt fumes (Couper, 1977; Schweyer, 1975; Dorrence and Petersen, 1969; Knotnerus, 1967), petroleum pitch volatiles (Greinke and Lewis, 1975), and air samples (Lao et al., 1973, 1976), and for the identification and quantitation of PAH (Duswalt and Mayer, 1970; Popl et al., 1976; DeMaio and Corn, 1966; Dicorcia et al., 1976; Zoccolillo et al., 1972; Bhatia, 1971). GC has also been used in the separation and analysis of PAH in coal tar pitch and coal tar pitch volatiles (Maher, 1968; Stroemberg and Widmark, 1970; White, 1975), petroleum, mineral oil, and coal tar (Lijinsky et al., 1963) and soot samples (Wallcave, 1969), and for the chemical standardization and quality assurance of whole crude coal tar (Gruber et al., 1970).

However, GC has certain limitations, such as requiring a cold finger for effective trapping of hot gaseous effluent (White, 1975), plumbing that has to be recalibrated regularly, and loss in the sensitivity of the flame ionization detector (FID) or electron capture detector (ECD) in order to provide sufficient effluent to the trap (Thomas and Lao, 1977). Also, FID or ECD will discriminate only to the extent of the variation in the response factor, which is only slight among PAH isomers, and therefore isomers are not well resolved. Lastly, in order to elute some PAH, a high column temperature and/or a long retention may be needed which may cause decomposition and/or a long analysis time.

Dexsil series GC (300 and 400) and capillary columns are among the best that are used for the analysis of complex mixtures of PAH in environmental samples (White, 1975). Separations of benzo(e)pyrene (BeP) and perylene from benzo(a)pyrene (BaP) and benz(a)anthracene from chrysene are poor or incomplete. Others that have been used are the SE-30, OV-7 and OV-17 columns. Nematic liquid crystals have been developed (Zielinski et al, 1976; Janini et al., 1975, 1976) to improve PAH separation. The stability, reliability, and resolving ability of these columns are still under investigation.

Gel Permeation:

Gel permeation chromatography is normally performed following solvent extractions and/or precipitations.

Gel permeation is used to separate asphalt into various fractions in order to study its composition (Schweyer, 1975; Couper, 1977) and to isolate PAH in heavy end petroleum distillates (McKay and Latham, 1973; Cogswell et al., 1971; Altgelt and Gouw, 1975; Jewell et al., 1974).

Ion Exchange:

Ion exchange is widely used in analyses of heavy end petroleum distillates for their acidic and basic components (Altgelt and Gouw, 1975; Jewell et al., 1972a) and in the separation of metals from tobacco smoke condensate (Finelli et al., 1972).

Paper:

Paper chromatography has been used to effect separations not accomplished by column chromatography or in conjunction with column chromatography. However, standards must be run simultaneously with each sample, the acetylated paper used is often contaminated and irregular in quality, and recovery is not quantitative. This technique is not reliable for the separation of complex mixtures (Katz and Monkman, 1964). Paper chromatography has been used to separate PAH, phenols and bases from coal tar pitch fractions (Masek, 1964; Macak and Rehak, 1962; Leibnitz et al., 1958).

2. Identification Methods

The identification and quantitation of PAH found in coal tar pitch, coal tar pitch volatiles, asphalt, and asphalt fumes are carried out using analytical tools such as infrared, ultraviolet, fluorescence, and phosphorescence spectroscopy, nuclear magnetic resonance and mass spectrometry, and atomic absorption spectrophotometry. These tools are used after separation and isolation of PAH and metals from various complex fractions into small concentrated samples, using the separation schemes described in Section IV.B.1. and Chapter I. A number of these methods have been interfaced with various types of chromatographic techniques to facilitate the characterization of metals and PAH.

a. Infrared Spectroscopy (IR)

Infrared spectroscopy (Silverstein and Bassler, 1967) has been used to characterize and identify the functional groups of organic compounds and chelated metals in coal-derived materials and asphalt samples (Schweyer, 1975, Couper, 1977; Wehry and Mamantov, 1977). Recent developments in matrix isolation of fourier transform IR spectroscopy (Wehry et al., 1976; Wehry and Mamantov, 1977) will improve the detection limits and the quantitation methods in the analysis of PAH in mixtures. IR has been used to analyze heavy residual oils (Kawahara, 1969), asphalts (Dorrence and Petersen, 1969), and the following components of coal tar pitch fractions: aromatics (Rao et al., 1960), acids and bases (Karr et al,, 1970), neutral oils (Maher, 1968), paraffins (Maher, 1968), phenols and quinolines (Karr et al., 1958, 1959).

b. Fluorescence and Phosphorescence Spectroscopy

PAH all have characteristic fluorescence and phosphorescence spectra, lifetime quantum yields and rate constants (Berlman, 1965; Becker, 1969; Zander, 1968). Fluorescence and phosphorescence techniques (Morgan et al., 1977; Schwarz and Wasik, 1976; Farooq and Kirkbright, 1976) are 1000-fold more sensitive than UV spectroscopy, allowing fluorescence excitation spectra to be recorded at much lower concentrations than the corresponding UV spectra. In addition, compounds can be selectively monitored in a mixture of two or three

PAH without interference from the other PAH. By selection of optimal emission or excitation wave lengths, differential techniques can be used to resolve overlapping PAH spectra. More recent developments using matrix isolation fluorescence and room temperature phosphorescence will aid in the analyses of PAH. Matrix isolation techniques using gaseous solvents will aid in alleviating difficulties of overlap of excitation and/or emission spectra of different PAH and energy transfer and quenching phenomena (Wehry and Mamantov, 1977). Phosphorescence of PAH adsorbed on a variety of surfaces at room temperature would alleviate the use of frozen matrix and/or degassed samples (Vo-Dinh, 1977).

These optical techniques have been used (1) to detect and characterize PAH utilizing the Shpol'skii effect at 77°K (Farooq and Kirkbright, 1976), (2) to determine concentrations of PAH in aqueous systems (Schwarz and Wasik, 1976), and (3) to correlate the carcinogenic potential of PAH with their fluorescence spectra (Morgan et al., 1977). Fluorescence techniques have also been used to analyze PAH from air samples (Fox and Staley, 1976; Slavin et al., 1977; Lannoye and Greinke, 1974), shale oil (Hurtubise et al., 1977), high boiling petroleum distillates (McKay and Latham, 1972), asphalt (Schweyer, 1975; Couper, 1977), and coal tar and coal tar pitch (White, 1975).

The major drawbacks of fluorescence techniques are the high background levels, interference from nonfluorescing material, quenching, self adsorption and photodecomposition. The high background can be due to other fluorescent compounds in the mixture, dirty glassware, or fluorescent impurities in the solvent. Therefore solvents must be redistilled or spectroanalyzed for fluorescent impurities and the cuvettes should be treated with concentrated nitric or hydrochloric acid. A major improvement in the field of fluorescence is the marketing of fluorescence units which give corrected spectra that are independent of lamp output, monochromator grating artifacts, and phototube response. The spectra generated are independent of instrumentation and can be compared to spectra of other laboratories. The fluorescence excitation spectra will be the same as UV spectra at 10^3 lower concentrations.

c. Mass Spectrometry (MS)

Mass spectrometry (Burlingame et al., 1974; McLafferty, 1973; Silverstein and Bassler, 1967) is utilized in the characterization of PAH at the nanogram level after chromatographic techniques and other identification methods have been used. This method is usually the last technique used in the positive identification of PAH. Before mass spectrometry can be used, the sample has to be fairly pure because of the difficulty in determination of isomeric PAH of similar molecular weight, such as BeP and BaP. The most common chromatographic technique used in conjunction with MS has been gas chromatography, but with the rapid advances being made in the area of HPLC, this technique may eventually supplant GC or at least be as widespread (McFadden et al., 1976; McLafferty et al., 1975; Jones and Yang, 1975; Elbert et al., 1976). The analysis of mixtures has been facilitated greatly by recent advances in minicomputers for data reduction and data acquisition and by the availability of chemical ionization and electron impact sources as one unit on both the quadrapole and magnetic mass spectrometry instruments.

Mass spectrometry has been used in the analysis of PAH in air pollutants (Lao et al., 1973, 1976), tobacco tar (Lee et al., 1976), heavy end petroleum oils (Jewell et al., 1974; Altgelt and Gouw, 1975), petroleum pitch volatiles (Greinke and Lewis, 1975), asphalt and asphalt fumes (Schweyer, 1975; Couper, 1977), coal tar distillates and residues (Shultz et al., 1967, 1972), coal derived fuels (Sharkey et al., 1975), and sediment and combustion products (Hase et al., 1976).

The spark source mass spectrometry technique (Lett et al., 1977) permits analysis for a large number of metals in a sample. This technique has the advantage of being able to provide data on the metal content of most samples down to 0.1 ppm with minimal sample preparation.

d. Nuclear Magnetic Resonance Spectrometry (NMR)

Carbon-13 NMR spectrometry (Silverstein and Bassler, 1967) is being applied to heavy end petroleum fractions in order to provide evidence for average structures of molecules present (Jewell et al., 1974). Proton coupled carbon-13 NMR provides rapid determinations of series of average parameters of aromatic hydrocarbons. Proton NMR spectra are not as valuable as proton coupled carbon-13 NMR spectra when analyzing for PAH in mixtures (Retcofsky et al., 1977). NMR techniques have been used to analyze complex mixtures, such as gasoline (Myers et al., 1975), asphalt fractions (Keefer et al., 1971; Schweyer, 1975; Couper, 1977), heavy end distillates (Coleman et al., 1973; Jewell et al., 1974), and coal tar pitch fractions (Fujiwara and Wainai, 1961). They have also been used in identification and characterization of isomeric PAH (Duswalt and Mayer, 1970), PAH (Brooks and Stevens, 1964), paraffins (Kochloefl et al., 1963) and aromatics in coal tar pitch fractions (Rao et al., 1960), and as a tracer tool in coal liquefaction processes (Schweighardt et al., 1976).

e. Ultraviolet Spectroscopy (UV)

UV is used routinely to characterize PAH compounds separated by chromatographic techniques from complex mixtures, basically because many UV spectra of PAH are available in the literature (Clar, 1964; Friedel and Orchin, 1951; Orchin and Jaffe, 1962). This technique is highly reproducible and facile. UV is very specific for individual compounds, so that in some instances where two PAH are not resolved by chromatography but have different absorption regions, the contributions of each can be determined, e.g. BeP and perylene. However, UV spectroscopy is not good in general for analyzing PAH in mixtures because of the interferences due to each PAH, the high background, and lower sensitivity than fluorescence. The use of non-absorbing solvents such as cyclohexane, pentane, methanol and ethanol limits the solubility of the PAH.

Recent developments in second derivative absorption spectrometry, however, show promise of being able to analyze a rather complex mixture of PAH without prior chromatographic separations (Hawthorne and Thorngate, 1977). This technique, which is still under investigation, will monitor the more volatile PAH in the vapor phase as well as the less volatile PAH in solvents. UV spectroscopy has been used to characterize the following materials separated from "coal tar pitch volatiles" extracts (Sawicki et al., 1974; White, 1975): BaP (Stroemberg and Widmark, 1970), PAH (von Lehmden et al., 1965; Sawicki et al., 1970a), neutral pentane soluble fractions of asphalt (Brooks and Stevens, 1964), and quinolines (Vahrmen, 1958). It has also been used to analyze petroleum pitch volatiles (Greinke and Lewis, 1975) and asphalt samples (Schweyer, 1975; Couper, 1977).

f. Other Techniques

Atomic Absorption Spectrophotometry (AA) is used in the analysis of metals from coal tar and coal tar pitch (Schulte et al, 1974; White, 1975) and asphalt and asphalt fumes (Schweyer, 1975; Couper, 1977). However, computer programs are needed to make the proper corrections for the interference of other metals not being analyzed; otherwise, the number of interference standards which must be prepared becomes unwieldy. More recent developments in the area of inductively coupled plasma-optical emission spectroscopy (Fassel and Kniseley, 1974) allow true simultaneous multielement analyses on a practical basis (30 metals).

It has been demonstrated that all metals and metalloids can be determined at the ultratrace level on μl or μg samples. All of the data accumulation on a simultaneous basis with minimal interelement and data reduction is handled easily by available computers.

Electron Spin Resonance (ESR) has been used to study organic compounds and in particular to characterize PAH (Bartle and Smith, 1967) in coal tar and asphalt (Schweyer, 1975).

X-ray Excited Optical Luminescence is a potential analytical tool (D'Silva *et al.*, 1976, 1977) for detecting and quantitating PAH at ultratrace levels (ppb). This technique is still under development.

3. Discussion of Existing and Proposed Analytical Methods

After the initial separation methods have been completed, a wide variety of analytical methods which combine chromatographic and spectroscopic techniques have been used in the difficult analyses for a number of PAH from complex mixtures which may contain over 100 different PAH. The most common methods which are described in this section have wide application, but have been most heavily used in the analysis of PAH in coal tar pitch, coal tar pitch volatiles, and organic material in the urban atmosphere. These same methods, although not developed for asphalt and asphalt fumes *per se*, are readily applied to the analysis of PAH in these mixtures.

Column chromatography/UV-VIS spectroscopy:

This method, which combines gravity fed chromatography with UV and visible spectroscopy (VIS), has been used to analyze for PAH in atmospheric particulate matter (Sawicki *et al.*, 1970a) and in air polluted by coal tar pitch fumes (Sawicki *et al.*, 1962, 1965). It can also be used to analyze for PAH from coal tar pitch, asphalt and asphalt fumes. This method, which has quantitated PAH and their heterocyclic analogues in the microgram range, has been used to analyze for such compounds as anthracene, phenanthrene, benz(a)anthracene, fluoranthene, pyrene, BaP, BeP, benzo(ghi)perylene, anthanthrene, coronene, dibenz(a,h)acridine, and dibenz(a,j)acridine (Sawicki et al., 1964, 1965). However, this method employs a slow chromatographic technique which requires arbitrary decisions for the cut of each fraction due to variable retention times. A number of days or weeks can be required for the analysis of PAH. Additionally when small quantities are present (below μg range), or when two or more compounds are not separable and have the same absorption, UV-VIS will not be useful as a detection technique.

Column chromatography/fluorescence spectroscopy:

The combination of gravity fed solid-liquid chromatography with fluorescence spectroscopy has been used to analyze atmospheric particulate matter for compounds such as those described in the preceding paragraph (Sawicki et al., 1970b,c). When applied to the analysis of PAH from coal tar pitch and asphalt sources, it is an improvement upon the preceding method, since it can be used to quantitate PAH in the nanogram range (1000-fold more sensitive) and to analyze for two or three PAH that co-chromatograph. However, this method suffers from the need for arbitrary decisions for the conclusion of each cut (fraction) due to variable retention times and from the long time needed for the chromatographic separations and analyses of PAH. The fluorescence aspect of the method has to consider instrumentation artifacts such as variations in lamp output, phototube response, monochromator grating and photodecomposition of the PAH.

Thin-layer chromatography/fluorescence spectroscopy:

Thin layer chromatography has been combined with fluorescence spectroscopy to analyze for BaP in bitumens, plants, airborne particulates, various source effluents including coal tar pitch volatiles (Sawicki et al., 1970d,e;

Lannoye and Greinke, 1974; Schamp and Von Wassenhove, 1972; Jackson et al., 1974b) and atmospheric isomeric PAH (Pierce and Katz, 1975). The analysis for BaP can be quantitated on a 10 µg to 0.01 µg range depending on the particular procedure used. However, this method is hampered by the loading factor, limited efficiency of separation and poor reproducibility. These problems can be overcome with pure standards and solvents and with TLC plates that are prepared and activated under the same conditions with known maximum loading efficiency to prevent streaking of plates.

A more recent modification has utilized adsorption and partition TLC in a two step process in conjunction with fluorescence spectroscopy to analyze for 12 isomeric PAH (Pierce and Katz, 1975). It has been possible to separate the PAH into 5, 6 and 7 ring compounds (Pierce and Katz, 1975), but this method further separates isomeric 5 or 6 ring compounds into individual components. This simple and rapid method has quantitatively resolved five pentacyclic, two C_{22} hexacyclic and five C_{24} hexacyclic PAH: BeP, BaP, benzo(b)fluoranthene, benzo(h)fluoranthene, perylene, dibenzo(def,mno)chrysene, benzo(ghi)perylene, naphtho(1,2,3,4-def)chrysene, benzo(rst)pentaphene, dibenzo(b,def)chrysene, naphtho(2,1,3-gra)naphthacene and dibenzo(def,p)chrysene.

Gas chromatography/UV spectroscopy:

Gas chromatography (FID or ECD) has been used with UV spectroscopy to examine coke oven effluents (Sawicki et al., 1974) for PAH such as fluoranthene, pyrene, benz(a)anthracene, chrysene, BaP, and BeP. It has also been used to analyze petroleum pitch volatiles for PAH such as methyl substituted chrysenes, phenanthrene and pyrenes, pyrene, BaP, BeP, chrysene and benz(a)anthracene (Greinke and Lewis, 1975). The detection limit for the PAH by this method is 0.5 to 0.1 µg per compound.

The potential difficulties with this method are the requirements for trapping of PAH by use of a cold finger, a split in the plumbing, which has to be recalibrated regularly, a decrease in the detection limits of the FID or ECD detectors in order to provide sufficient effluent to trap, and pyrolysis of PAH at high temperatures (Thomas and Lao, 1977). The FID or ECD detectors, which discriminate only to the extent of the response factor, vary only slightly among isomers, and therefore the addition of UV spectroscopy will aid in the quantitation of two co-chromatographic compounds with different absorption wave length maxima, e.g. BeP and perylene. UV spectroscopy is not useful, however, much below the microgram level.

Gas chromatography/fluorescence-phosphorescence spectroscopy:

This method, which is an improvement upon the GC-UV method, combines gas chromatography (ECD) and fluorescence spectroscopy. It has been used to analyze PAH in coal tar, coal tar pitch and coal tar pitch volatiles (White, 1975) and can be applied to asphalt to quantitate PAH in the ng range (1000-fold more sensitive than GC-UV) and several PAH that co-chromatograph. Some of the PAH that have been analyzed are pyrene, chrysene, BaP, BeP, benz(a)anthracene, benzo(h)fluoranthene and perylene. As indicated in the previous paragraph, the GC aspect of this method suffers from a number of potential problems which must be taken into account. The instrumentation artifacts due to the fluorescence-phosphorescence unit can be corrected by daily calibration of the unit with standards in degassed emission tubes and then use of degassed samples for analysis. Both standards and samples need to be trapped by GC to avoid introducing other variables. With the advent of improved instrument technology, the corrections for instrumentation artifacts are now incorporated in the fluorescence units. Photodecomposition of PAH, however, is still a potential problem. A slightly different method (Burchfield et al., 1971) increases the sensitivity by use of gas phase fluorescence detection instead of electron capture detection. Gas phase measurements are more convenient to make and less susceptible to light scatter by solvents. The fluorescence intensity is lower but can be increased by using an ellipsoidal condensing mirror housing. The instrumentation artifacts and photodecomposition still need to be taken into account. Analyses have been carried out for compounds including fluorene, anthracene, triphenylene, BaP, dibenz(a,h)anthracene, perylene, chrysene, pyrene, fluoranthene, and benzo(ghi)perylene.

High pressure liquid chromatography/UV or fluorescence spectroscopy:

A combination of HPLC with UV or fluorescence has been used to analyze for as many as 17 PAH in atmospheric particulate matter (Fox and Staley, 1976; Dong *et al.*, 1976), BaP in coal tar pitch volatiles (Boden, 1976) and PAH in engine oils (Vaughan et al., 1973). This method has also shown potential use in the analysis of fossil fuels for PAH (Thomas and Lao, 1977) and has a very wide potential application in the analysis of all complex mixtures.

In addition to the fact that the potential difficulties of GC do not apply to HPLC, the HPLC samples are collected at room temperature in non-fluorescent solvents without decomposition. Larger samples can be introduced (up to 3 mg) at the column head and the effluent can be stored in the cold or analyzed immediately by UV or fluorescence detectors. Proper selection of optimal fluorescence excitation or emission wavelengths or of maximum absorption wavelengths can permit analysis for two or possibly three PAH that co-chromatograph. The use of HPLC-fluorescence provides a more sensitive and selective method than HPLC/UV because of the natural strong fluorescence of PAH. The sensitivity of the method allows the quantitation of PAH in the 10 to 100 picogram range, using the flow cell connected to the detector and the stop flow technique which permits the use of variable wavelength detectors. The only major potential problem that might arise from this method is lack of knowledge of the limitations of the detectors.

Gas chromatography/mass spectrometry:

This method, which combines gas chromatography with mass spectrometry and computer, has long been preferred for the analysis of complex organic mixtures. It has been used to analyze PAH content in airborne pollutants (Lao et al., 1973, 1976; Karasek et al., 1978), in sediment and combustion systems (Hase et al., 1976), in coal tar distillates and in residues (Sharkey et al., 1975). The system of choice according to one investigator (Lao et al., 1976) is the use of GC-FID-quadrapole MS-computer in analyzing for PAH in air samples. The detection limit of GC-MS varies with the MS unit, from ng to pg range.

Sample preparation, extraction and sampling should be carried out with care to prevent any contamination. Computerized data accumulation and reduction allows for subtraction of spectral background to prevent misinterpretation of mass spectra and for the analysis of a large number of PAH in any one sample (Lao et al., 1976; Hase et al., 1976). The availability of pure reference materials is important for all of these determinations.

High pressure liquid chromatograph/mass spectrometry:

In this method, which is still in the experimental stage, HPLC is combined with MS and computer (Jones and Yang, 1975; McLafferty et al., 1975; Elbert et al., 1976). This method will be ideal for the analysis of PAH from asphalt and coal tar pitch sources. An efficient interface system is still under development. The protopype interface (McFadden et al., 1976) is not efficient and at present is far inferior to GC-MS. However, development of a better interface will eventually make the application of

HPLC-MS more efficient and convenient than GC-MS for PAH (Thomas and Lao, 1977). In addition to the analysis of a large number of PAH in any one sample by use of computerized data accumulation and data reduction of mass spectral values, the HPLC will afford better separation and resolution, little or no decomposition at room temperature, larger samples of PAH in general and isomeric PAH in particular when compared to GC.

Other methods:

An integrated method (Jewell et al., 1974) which has been used for semi-quantitative characterization of residual oils has potential application in the analysis of PAH from asphalt. This method incorporates sophisticated chromatographic techniques which separate the maltene fraction into resins, oils, saturates and aromatics. Molecular sieves are used to separate n-paraffins from other saturates. Gel permeation, GC, TLC, elemental analyses, IR, UV, NMR, ESR and MS procedures are then used to characterize the types of functional groups, quantity and types of chain and aromatic ring structures and heteroatom distribution in the subfractions.

C. Monitoring

Monitoring of asphalt fume and coal tar pitch volatiles in the workplace and in emissions into the environment requires special techniques of sampling and analysis. The sample collected must accurately represent the complex material investigated, and the material being analyzed must be related to the biological effects which are of concern.

Monitoring procedures for urban air (Dong et al., 1976; Fox and Staley, 1976; Pierce and Katz, 1975; Lannoye and Greinke, 1974; Lao et al., 1973), water (Zafiriou, 1973; Warner, 1976), soil (Giger and Blumer, 1974), and occupational environments (Bjørseth and Lunde, 1977; Ball et al., 1976; Greinke and Lewis, 1975; White, 1975) need to be performed rapidly and reproducibly by technicians using standardized and relatively inexpensive equipment. The monitoring of the occupational and urban environments requires both high and low volume samplers, i.e., environmental and personal monitoring. The effectiveness of the sampling procedure is influenced by a number of factors such as the nature of the filter, the air velocity, and the sampling rate. These factors which are considered in the selection and use of monitoring procedures have been discussed by White (1972, 1975) in relation to coke oven emissions. Of the analytical methods discussed in Section IV.B.3., GC-FID-quadrapole MS-computer is best suited to the needs of monitoring procedures at present. The HPLC-MS-computer method will, however, be the analytical choice of the future.

V. TOXICITY AND CLINICAL STUDIES IN MAN

Toxic effects of bituminous materials on humans have long been noted. Effects on specific target organs, particularly skin, eyes, and respiratory system, are described in Section A. The effects of various forms of exposure to asphalt, pitch, and combinations of these materials are discussed in Sections B and C. The effects of coal tar medications are considered in Section D.

A. Effects on Organ Systems

1. Effects of asphalt

a. Effects on the skin:

Almost no reports of clinical effects of asphalt without coal tar have appeared in the literature. Some cases of dermatitis related to asphalt exposure were mentioned by Baylor and Weaver (1968). The National Safety Council (1974) suggests precautions in handling asphalt to avoid inflammation and dermatitis. A single case of squamous cell carcinoma following long exposure to native lake asphalt road materials was reported by Henry (1947).

b. Effects on the respiratory system:

Some increase in noncancerous respiratory disease, chiefly chronic bronchitis, was reported by Baylor and Weaver (1968) in a survey of petroleum refinery and other workers exposed to asphalt, as compared to unexposed controls.

Respiratory symptoms including bronchitis, chronic cough, nose and throat inflammation and congestion, and laryngitis were described by Zeglio (1950) in workers exposed to native asphalt, possibly sometimes adulterated with pitch.

2. Effects of coal tar pitch

a. Effects on the skin:

A number of skin changes have been observed following exposure to pitch alone or combined with asphalt or other factors. Most of the classic detailed descriptions are found in the early literature (Oliver, 1908; Schamberg, 1910; Foerster and Schwartz, 1939; Henry, 1947; Ross, 1948; Fisher, 1953; Combes, 1954; Eckardt, 1959) and continue to be cited. More recent descriptions have also appeared (Lev et al., 1966; Hodgson and Whitely, 1970; Hervin and Emmett, 1976b). Based on these references, the biological effects of coal tar pitch on human skin can be summarized as follows:

Tar or pitch burns: Burns from hot pitch or tar are relatively common (Barry et al., 1975). Burn scars and other areas of epidermal atrophy may be sites for later skin cancer (Swanbeck, 1971).

Allergic eczematous dermatitis: Allergic reactions occur in occupational exposures, but more commonly result from use of coal tar medications.

Folliculitis, comedones, acneform lesions: These common lesions, occurring after one month of exposure, are usually limited to the face, neck, and upper limbs, but may also appear in areas such as the thighs which are abraded by clothing. Sebaceous cysts may appear on the scrotum. These lesions are attributed to blockage of follicles with tar and pitch and to induced keratin production in the pilosebaceous unit. Spontaneous remission occurs when exposure ceases. These effects can be reduced substantially with preventive measures and good personal hygiene.

Tar erythema (photosensitization, "pitch smarts"): Crude coal tar and coal tar pitch are photosensitizing (phototoxic) agents. Combined exposure to dust or fumes from tar and pitch and to sunlight (actinic radiation) results in a painful, stinging condition characterized by an immediate eruption of wheals (urticaria) and reddening (erythema) followed by epidermal injury. After several episodes of phototoxic reactions, chronic hyperpigmentation may occur. The photosensitization reaction usually begins within an hour of exposure to light and pitch, and may continue for many hours after exposure. In some cases, reexposure to sunlight in the absence of pitch within the next several days will result in burning. The face, neck, and forearms, which are usually exposed, are most commonly affected. Peeling occurs in three to five days, even in the absence of erythema. Exposure to high humidity, sweating, high concentration of fumes (especially from overheating of pitch), wind, and strong sunlight all seem to intensify the phototoxic reaction. Use of low fume ("no burn") pitch is said to diminish the reaction.

Chronic hyperpigmentation (pitch melanosis): Chronic melanosis, or darkening of the skin, may develop after five or more years of exposure to coal tar pitch, and may accompany other skin changes. Melanosis may follow repeated phototoxic episodes, but may also affect unexposed areas. Hypopigmentation occasionally follows chronic pitch photosensitization.

Chronic tar dermatosis ("shagreen skin"): This condition, an essentially irreversible process affecting the forearms, back of neck, face, and hands, usually requires at least ten years of exposure. Manifestations may include keratin hyperplasia, effects of repeated photosensitization, telangiectasia, pigment changes, and neoplasia (papillomas and keratoses.)

Neoplastic changes: Exposure to coal tar and coal tar pitch can result in a variety of benign and malignant growths, principally on exposed skin surfaces but often affecting the scrotum. Lesions associated with pitch exposure include:

Benign:

Keratoses and papillomas, basal or squamous-cell - horny growths, fibroepithelial papillomas (skin tags), simple warts ("tar molluscum").

Keratoacanthomas - pitch acanthomas, pitch warts - often accompanied by other proliferative lesions; sometimes misdiagnosed as squamous cell carcinomas; sometimes considered precancerous; often regress spontaneously.

Keratoses may develop within six months; papillomas and keratoacanthomas may develop as soon as six months or as long as 41 years after initial exposure. A study of excised pitch warts maintained in tissue culture indicated that, although a high degree of polyploidy was associated with the cultured warts, the chromosomes were normal (Everall *et al*., 1967).

Malignant:

Squamous cell carcinomas - epidermoid carcinomas, spinocellular or prickle cell epitheliomas - can develop within 18 months to 34 years.

Basal cell carcinomas - basal cell epitheliomas, rodent ulcers - uncommon.

b. *Effects on the eyes:*

Acute or chronic symptoms of eye exposure to pitch have been reported by Moret (1912), Foerster and Schwartz (1939), Fisher (1953), Barkov and Prosetskii (1958), Crow *et al*. (1961), Lev *et al*. (1966), Gmyrya *et al*. (1970), Susorov (1970), Hervin and Emmett (1976a,b), and Emmett *et al*. (1977).

Acute episodes of eye involvement from either pitch fumes or pitch dust usually begin two to four hours after initial exposure (beginning of work shift.) Symptoms may include reddening of the eyelids and conjunctiva, perhaps accompanied by swelling and spasms of the lids, and disturbed vision. After exposure has stopped, symptoms continue to increase; within about twelve hours the eyes may be matted shut, with a purulent discharge. In mild cases, symptoms disappear within three days, although photophobia may continue for one to two months in the absence of further pitch exposure. Attempts to reduce the severity of the response may include wearing protective glasses and working at night. Eye involvement may be minimized by reducing exposure to pitch volatiles to levels below 0.2 mg cyclohexane solubles per cubic meter. In dusty operations involving pitch, no signs of conjunctivitis were observed at levels of cyclohexane solubles below 0.11 mg/m^3.

Prolonged exposure to pitch dust or volatiles may result in chronic conjunctivitis and corneal staining, reduction in dark-adaptation and in corneal sensitivity leading to corneal anesthesia, restriction of the visual field, and pterygia.

c. Effects on the respiratory system:

Exposure to coal tar pitch dust has been noted to result in acute upper respiratory distress, such as nasal congestion, hoarseness, throat irritation and swelling, and coughing reported by Susorov (1970) and Lev *et al.* (1966). Increased mortality from chronic bronchitis, emphysema and lung cancer have been reported in workers exposed to coal tar pitch volatiles (National Research Council, 1972; Hueper, 1963; Hammond *et al.*, 1976; Doll *et al.*, 1965; Konstantinov and Kuzminyuk, 1971; Redmond *et al.*, 1972; Lloyd, 1971; Okubo and Tsuchiya, 1974; Sakabe *et al.*, 1975).

d. Other effects:

Exposure to coal tar pitch has been related to disorders of various organs. Functional stomach disorders including chronic gastritis in pitch workers have been described by Mikheeva (1967). A greater risk of dental caries, leukoplakia and edema of the oral mucosa has been noted in tar and pitch workers (Pekker, 1967).

Increased incidence of cancer of a variety of organs has been observed in persons whose exposures included coal tar pitch. Sites include bladder (Henry, 1947 ; Borneff, 1965; Zorn, 1966; Doll et al., 1972; Hammond et al., 1976), kidney (Redmond et al., 1972), stomach (Hammond et al., 1976; U.S. National Institute for Occupational Safety and Health, 1973), intestine (Lloyd, 1971), pancreas (Lloyd, 1971), larynx (Hammond et al., 1976; Guardascione and Cagetti, 1962), and buccal cavity, pharynx, and esophagus (Hammond et al., 1976).

Most pitch workers are also exposed to other potentially carcinogenic materials such as coke oven emissions (Lloyd, 1971; Redmond et al., 1972), or lower-boiling fractions of coal tar such as basic fractions or creosote (Doll et al., 1972). Also, the influence of coal tar pitch may be modified by other factors such as smoking history or exposure to sunlight or other ultraviolet light (Bingham et al., 1976; Emmett, 1973, 1975).

Bladder cancer is generally thought of in relation to exposure to aromatic amines which are present in appreciable quantities in some of the lower-boiling fractions of crude coal tar, but are not major components of coal tar pitch. For instance, Doll et al. (1972) reported the case histories of 12 men who died from bladder cancer after being employed in gas works. However, a few cases appear to involve exposure only to coal tar pitch. Borneff (1965) reported a case history of a 62-year old tar distillery worker with no known work contact with aniline or other low-boiling tar fractions, who had pitch warts for several years preceding symptoms of bladder cancer. A case of bladder cancer in a road worker with exposure only to paving tar and asphalt was reported by Zorn (1966), who identified alpha- and beta-naphthylamine in the "paving tar" (pitch). In both cases the workers had been exposed about 15 years before developing symptoms of bladder cancer. In neither case did the men smoke or have known chronic exposure to any potential carcinogen except pitch and tar.

B. Effects of Occupational Exposure

As early as 1775, Percival Pott recognized that the scrotal cancer of chimney sweeps was a result of occupational exposure to soot. More recently, Henry (1947) assembled data relating cases of skin cancer reported in Britain from 1920 through 1945 to numerous occupational exposures, many of which included coal tar and similar materials.

In evaluating the carcinogenic potential of asphalt, coal tar pitch and similar materials, it is important to consider the multiple factors which may contribute to potency (Bingham et al., 1976). Ultraviolet radiation (UV), itself generally considered to be carcinogenic (Emmett, 1973, 1975), may augment the carcinogenicity of PAH in pitch or other bitumens, The relationship of photosensitization to development of cancer is not known. On the other hand, the action of UV, or of carcinogens present in bitumens may be modified by other components which may act as cocarcinogens or as inhibitors. Such compounds may be PAH or heterocyclic aromatics closely related to the carcinogens, or phenolic or other materials whose role is not yet clearly understood. In addition, other environmental factors, such as smoking and polluted air, may have an important influence on the carcinogenicity of bitumens.

1. Exposure to asphalt

a. Refineries:

Baylor and Weaver (1968) surveyed the health of 462 asphalt workers in 25 petroleum refineries and of 379 controls. Each worker had been engaged in asphalt work for at least five years, the average being 15.1 years. No significant differences in health were found, although there was some dermatitis and other noncancerous skin disease, none severe, and an increased incidence of chronic bronchitis and other noncancerous lung disease in the asphalt workers.

In a study of Russian refineries, Kireeva and Yanysheva (1970) found the highest levels of BaP around areas where higher boiling crude oil fractions were being further processed. BaP concentrations reached 2.58 $\mu g/m^3$ in the asphalt processing area and 36.59 $\mu g/m^3$ in the asphalt coking area. Other PAH identified in these two areas were dibenz(ah)anthracene, benz(a)anthracene, dibenz(ac)anthracene and anthracene. Of these, dibenz(ah)anthracene is considered a strong carcinogen, anthracene is noncarcinogenic, and the other two are weakly carcinogenic. The incineration of gases from the air blowing operation reduced the BaP concentration only from 1.1 $\mu g/m^3$ to 0.84 $\mu g/m^3$. (Kireeva and Yanysheva, 1970).

b. Other:

In 1947, Henry reported one case of squamous cell carcinoma in a man exposed for 22 years to native lake asphalt road materials. Zeglio (1950) described respiratory symptoms in most of 22 electrical insulation workers using native asphalt heated to 120°C. Symptoms, including bronchitis, chronic cough, nose and throat irritation, breathing difficulty, rhinitis, and laryngitis, improved when not working. Occasionally the asphalt may have been adulterated with pitch.

In connection with a survey of the health of asphalt workers in refineries, Baylor and Weaver (1968) assembled inforamtion about instances of ill health attributable to asphalt exposure related to paving or roofing work or driving over asphalt highways. Except for several cases of dermatitis and minor nasal irritation, no cases of asphalt-related disease were reported by 31 construction or paving companies, 15 state highway commissions and boards of health, three large roofing companies, four large trucking companies, and six insurance companies.

2. Exposure to coal tar pitch

In contrast to asphalt, exposure to coal tar pitch may result in clearly-defined biological effects.

a. Exposure during production of pitch:

During the production and processing of pitch-containing crude coal tars at coke ovens, tar distilleries, gas works, and other coal conversion plants, workers may be exposed not only to pitch, but to a variety of noxious gases, fumes, emissions, and lower-boiling tar fractions, as well as to sunlight and cigarette smoking. Because of the multiple factors involved in these exposures, the role of the pitch fraction in the production of biological effects is not clear. Epidemiological studies of coke oven workers indicate increased mortality from cancer of the lung (Lloyd, 1971; Redmond et al. 1972; Okubo and Tsuchiya, 1974; Sakabe et al., 1975; O'Connor, 1971), which is greatly increased by cigarette smoking (U.S. National Institute for Occupational Safety and Health, 1973). Increased incidence of cancers of the skin (Henry, 1947), kidney (Redmond et al., 1972), and certain other sites (Lloyd, 1971) have also been reported in coke oven workers.

An important relationship noted by Lloyd (1971) is that between the temperature of coal carbonization (thus, composition of volatiles) and mortality risk from lung cancer, as indicated in Table V-1. Mazumdar et al. (1975) have reported a correlation between exposure (length of time and work area) to coal tar pitch volatiles and development of cancer (particularly cancers of the respiratory system) in coke oven workers.

Measurements of levels of PAH, BaP, or benzene or cyclohexane soluble fractions of "coal tar pitch volatiles" (CTPV) have been made at coke, iron

TABLE V-1. TEMPERATURE OF CARBONIZATION AND REPORTED EXCESS OF LUNG CANCER

Temperature °C	Type of Process	Percent Excess Lung Cancer
400-500	Vertical gas works retorts	27
900-1100	Horizontal gas works retorts	83
1200-1400	Coke Ovens	255
1500 +	Gas generators (Japanese)	800

Source: Lloyd, 1971

and steel plants. However, it should be emphasized that the presence of such materials, which may be found in a variety of tarry residues such as tobacco smoke, charred food, asphalt fume, automobile exhaust, carbonized wood, and cracked petroleum residues, does not imply that any or all of the PAH are attributable to coal tar pitch.

Some PAH levels measured near coke, iron and steel complexes do appear to be related to the presence of pitch. When Masek (1971) sampled six Czechoslovakian coke plants, he found high levels of exposure of workers, especially oven workers, to BaP. Table V-2 presents the data collected at one of the coke plants (new at the time of sampling) which also carried on pitch processing, including pitch coking.

In early studies in Britain, numerous cases of cancer of the bladder (Henry *et al*., 1931) and skin (Henry, 1947; Fisher, 1953) were reported in workers at tar distilleries and gas works. Nonneoplastic skin changes were also reported in tar distillers (Fisher, 1953). In later studies of gas works employees, Doll *et al*. (1965, 1972) found increased risk of bronchitis and cancer of the bladder, lung, and scrotum in men with high exposure to volatiles from coal gasification. The risk of bronchitis appeared to be greater in vertical retort houses (400 to 500°C), while the risk of lung cancer was higher in horizontal retort houses (900 to 1100°C) (Doll *et al*., 1972).

Spectrophotometric analysis by Lawther *et al*. (1965) of cyclohexane soluble fractions of air samples taken in British retort houses revealed acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(e)pyrene, benzo(a)pyrene, perylene, anthanthrene, coronene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(ghi)perylene. The particulates were tarry droplets 0.1-1 μm in diameter. Continuous air and personal monitoring of coronene, BaP, BeP, and benzo(ghi)perylene in-

TABLE V-2. BaP CONCENTRATIONS AT A CZECHOSLOVAKIAN PITCH PROCESSING COKE PLANT

Sampling Point	Number of Samples	BaP Concentration ($\mu g/m^3$)		
		Minimum	Maximum	Average
Ascension pipes of pitch battery	35	0.386	12.958	2.550
Collecting main of pitch battery--machinery side	35	0.436	12.800	2.250
Collecting main of pitch battery--discharge side	35	0.406	15.900	2.259
Medium pitch pumping station	33	0.031	1.516	0.200
Tar distillation pumping station	33	0.106	0.923	0.400
Administration building (indoors)	33	0.005	0.407	0.082

Source: Masek, 1971

dicated that, although exposure levels varied widely within the retort house, all workers were exposed to PAH levels higher than normal urban levels.

Gmyrya et al. (1970) examined 152 coal tar chemical workers, the majority 26 to 45 years old, for signs of eye involvement from chronic tar and pitch exposure. Most had symptoms of chronic exposure. Dark adaptation was below normal in 71% of 112 workers tested. Disorders in corneal sensitivity appeared soon and progressed with years of work. Complete corneal anesthesia was observed in four eyes.

Mikheeva (1967) reported that half of 87 workers in the pitch department of a byproduct coke plant had disturbances in basic stomach functions. The incidence of functional changes was two to three times higher in pitch workers than in controls. The changes were attributed to the effect of pitch on the gastric mucosa.

In a study by Pekker (1967) the incidence of caries, leukoplakia and observable changes in the oral mucosa was higher in the 547 tar processing and coking workers than in controls from other parts of the plant. Free oxygen tension in the oral mucosa was 3 to 4 times lower in the tar workers.

In addition to the effects resulting from exposure to products of conventional coking of coal at coke ovens, gas works, and tar distilleries, tumors were also observed in workers in a pilot plant for the hydrogenation of coal (Sexton, 1960a,b). Samples of materials to which the workers were exposed also produced cancer in experimental animals (Weil and Condra, 1960). This study illustrates the fact that even with precautions for the health of workers, tarry residues and other products of new coal conversion processes may be hazardous to workers and users.

b. Exposure during use:

(1) Electrodes:

As described in Chapter III, certain metallurgical electrodes, principally the anodes used for primary aluminum manufacture, are made of carbonaceous material such as petroleum coke as filler, with a large proportion of coal tar pitch as a binder. During prebaking and use, thirty to forty percent of the pitch binder is volatilized, producing a major source of potential exposure to coal tar pitch volatiles. In an industrial hygiene survey by Larsen (1973), air samples taken near potlines using prebaked anodes had a range of total particulates from 0.90 to 8.96 mg/m^3 and a range of benzene solubles from 0.01 to 0.1 mg/m^3. Personal air samples ranged from 0.7 to 30.4 mg/m^3 for composite total particulates and from 0.0 to 0.5 mg/m^3 for composite benzene solubles. There is a tendency to replace the prebaked electrode with the self-burning (Soderberg) electrode, which has not been prebaked and thus releases all of its volatiles in the potroom during aluminum reduction. Concern has been expressed over exposure of potroom workers to coal tar pitch volatiles from the Soderberg electrode (Shuler and Bierbaum, 1974).

A study (Equitable Environmental Health, Inc., 1977) of the mortality of aluminum workers, carried out for The Aluminum Association, Inc., has provided epidemiological information that may be helpful in evaluating the health effects of exposure to coal tar pitch volatiles. Records of 23,033 men who had worked five years or more in aluminum reduction plants between 1946 and 1973 indicated a slight positive association between employment as a potroom worker and lung cancer, most evident in workers in the horizontal Soderberg process. Slight excesses of leukemia and lymphoma deaths in these workers were not statistically significant. A significant excess of deaths due to motor vehicle accidents was also observed in potroom workers. The report suggests that the role of coal tar pitch volatiles in the health problems of potroom workers should receive further study.

Konstantinov and Kuzminyuk (1971) examined mortality records over an 11-year period (1955 to 1966). Incidence of malignant neoplasms among furnace operators, anode operators and crane operators (all subject to exposure from the carbon anodes) was compared to the incidence in the population of the community in which the aluminum plant was located. As shown in Table V-3, workers in electrolytic shops that used Soderberg (self-burning) anodes had increased mortality from cancer of all sites and cancer of the lungs, bronchi and pleura. They also had an increased incidence of skin cancer. Workers at the shop using prebaked anodes showed no increased mortality. Levels of BaP at several shops utilizing different process technologies showed wide variation. The highest BaP levels (29.2 to 245 $\mu g/m^3$) were seen in a Soderberg shop with lateral current supply. Air-cooled anodes receiving overhead current released fewer fumes, and thus less BaP, than uncooled anodes receiving overhead current. No BaP was detected in the prebaked anode shop. Under all conditions, the highest levels of BaP were reached during furnace processing and replacement of butts.

Substitution of petroleum pitch (a cracked petroleum residue) for coal tar pitch in carbon anodes reduced BaP levels in the electrolytic shop. Dust levels of BaP were reduced 7 to 24-fold when a petroleum pitch with 11.6 times less BaP than coal tar pitch was used (Konstantinov _et al_., 1973).

TABLE V-3

INCIDENCE OF CANCER IN ALUMINUM WORKERS EXPOSED TO SODERBERG OR PREBAKED ANODES

	Type of Cancer	Age Group (Yrs.)	Factor of Excess Over Controls
Soderberg anode: (self-burning)	All Sites (mortality)	All	1.85
		18-39	7.15
		40 +	1.57
	Lungs, Bronchi, Pleura (mortality)	All	1.7
		18-39	8.3
		40 +	no excess
	Skin (incidence)	All	10.5
		18-39	38.8
		40 +	6.6
Prebaked anode:	All Sites (mortality)	All	no excess
		18-39	no excess
		40 +	no excess

Source: Konstantinov and Kuzminyuk, 1971.

(2) Patent fuel (briquettes):

Workers handling pitch-containing coal briquettes in the sunlight developed phototoxic reactions of the eyes and skin, as well as upper respiratory symptoms (Lev *et al*., 1966)

Henry (1947) reported 610 cases of squamous cell carcinoma in patent fuel workers out of 3753 cases of job-related skin cancer. In 1931, Henry *et al*. reported that the occupation of patent fuel laborer was one of the two occupations with the highest death rate from bladder cancer, the risk being four times greater than that for the male population of England and Wales.

Skin lesions in 144 patent fuel workers exposed to coal dust and pitch during 1957 to 1963, as compared to 263 controls (dermatological out-patients), were described by Hodgson and Whiteley (1970). Photosensitivity was recorded in 57% of the pitch workers and was unrelated to incidence of pitch warts or acne. All acneiform lesions were much more common in the pitch workers (93%) than in the controls (31%). There was little difference between the two groups in the incidence of benign proliferative lesions. Squamous keratoses were slightly more common in the pitch workers (12%) than in the controls (10%). Chronic tar dermatosis was found in 5% of pitch workers with pitch exposure of 30 to 50 years, but not in controls. Squamous cell carcinoma incidence was 2.8% in pitch workers compared with 0.4% in controls. Pitch acanthoma developed in about 10% of the pitch workers; incidence was related to duration of exposure, but also varied from 3 to 24% for low to high levels of skin contamination with pitch; spontaneous regression was noted in 26% of the cases. Scrotal proliferative changes were reported in 13.5% of all the pitch workers, with 3.5% incidence of keratoacanthoma and one squamous carcinoma. Although incidence of some proliferative lesions increased with increased exposure, the findings suggested that there is also a personal susceptibility to pitch.

(3) Other

Blast furnace refractory brick: Levels of BaP ranged from 7 to 2500 μg/m^3 near a blast furnace lined with pitch-bonded refractory brick containing up to 15% pitch. In a survey of workers at this plant, Kapitul'skii et al. (1971) found that 22% of 149 workers had rashes on hands, face and other parts of the body. None of the workers at another plant using less than 1% pitch in the refractory brick had such symptoms. Tanimura (1968) found high levels of BaP at several sites at an iron and steel complex. The presence of pitch-refractory bricks might contribute to BaP levels near the blast furnace, while tar or pitch used as a lubricant might have contributed to BaP levels near the pouring of steel into ingots or at the high mills. Pitch was used as an open hearth fuel and as a binder in electrodes used in the electric arc furnace, two other sites of BaP contamination.

Foundries: Levels of BaP at a Czech foundry were 1.2 μg/m^3 in air, 0.100-14.04 mg/kg in sedimented dust, and 4.8-28.6 mg/kg in floor sweepings containing coal tar. In an examination of 286 workers in two foundries for signs of exposure to high BaP levels, Kolomaznik et al. (1963) noted one case of lung cancer, nine laryngeal neoplasms, eight laryngeal pachydermas, ten cases of leukoplakia and five unspecified pre-cancerous conditions.

Molded articles: Crow et al. (1961) examined workers engaged in molding articles from pitch, asbestos and slate dust. Of the men exposed to pitch, seventy percent developed comedones and forty percent had folliculitis of the thighs. Seventy percent of the white workers reported pitch photosensitivity; forty percent reported photophobia. More than half the men reported chronic "sweating yellow", which continued for three to seven days during vacations and, in 25% of the workers, persisted up to two weeks after work exposure to pitch had ceased. Henry (1947) reported one case of squamous cell carcinoma in a man employed in the manufacture of clay pigeons.

Electrical conduits: Foerster and Schwartz (1939) reported that over half of the 500 men at four separate plants had hyperpigmentation (melanosis) or cutaneous lesions; comedones, folliculitis, keratoses, and papillomas were also common, and squamous cell carcinomas were noted. Henry (1947) reported that 55 out of 3753 cases of occupational skin cancer occurred in workers manufacturing or installing electrical equipment. Three cases of squamous carcinoma (two scrotal) occurring in a group of 200 workers engaged for more than five years in the process of "Stanford jointing" of earthenware pipes used as conduit for under ground electric cable were described by Spink et al. (1964). Although the jointing compound, which was applied hot, contained 20% coal tar, direct exposure was considered limited and the liquid tar was considered less hazardous than a dusty material. The cases were attributed to liberal skin contact with a solvent-refined, petroleum-derived spindle oil used to protect the pipe during jointing.

Pipe covering: Approximately ten workers were exposed to CTPV resulting from the manufacture of a pipe coating using pitch, powdered polyvinyl chloride and "petroleum tar." The benzene soluble fraction in personal air samples (breathing zone) ranged from 0.18 to 4.41 mg/m^3. Sixteen out of seventeen samples exceeded the OSHA standard of 0.2 mg/m^3 (see Chapter VII), five samples exceeded 1.0 mg/m^3, and ten out of sixteen were at least double the standard (Gunter and Ligo, 1976).

Carbon Products: After twelve years of observation of a relatively stable population of 170 workers making carbon products, Ross (1948) recorded a total of 66 persons with folliculitis, comedones and acne, 25 with hyperpigmentation, 26 with chronic tar dermatosis, 102 with papillomas, and 16 with squamous cell carcinoma.

Floor laying: Abaseev et al. (1975) described a floor laying procedure in which hot coal tar pitch was spread on concrete primed with anthracene oil, wooden boards were pressed into place, and cracks were filled with dry pitch applied with a hot iron (500°C). During this operation, the BaP levels in the air might reach 0.24 mg/m^3. Use of a catalytic after burner (at 400°C) on the trapped fumes eliminated the hazard.

Commercial fishing: Henry (1947) reported skin cancers in workers exposed to tar and pitch in fishing net repair and boat repair. Spitzer et al. (1975) noted that commercial fishermen who had worked longer than eight seasons had a 65% greater risk of lip cancer than other Newfoundland males of comparable age. Analysis of other risk factors (such as outdoor exposure and tobacco use) unexpectedly indicated that using the mouth as a "third hand" to control tar-coated nets reduced the risk of lip cancer by fifty percent.

3. Combined exposure to asphalt and coal tar pitch

a. Roofing:

During both the laying and the tearing off of large commercial roofs, workers are exposed to fumes and dust from both asphalt and coal tar pitch which are used in various layers of built up roofing. It is not possible to separate the contributions of the asphalt and the pitch to the "coal tar pitch volatiles" or to health effects on exposed workers.

Air samples were analyzed and roofers were examined in health hazard evaluations of the tearing off of an old roof (Hervin and Emmett, 1976a) and the laying of a new roof (Hervin and Emmett 1976b). During the tearing off operation, levels of cyclobexane solubles from personal air samples varied from less than 0.01 to 1.88 mg/m^3. Nine of fifteen men were exposed to more than the current OSHA allowable level for coal tar pitch volatiles (0.2 mg/m^3). The PAH levels in the cyclohexane fraction varied from 0.059 to 0.247 mg/m^3. Spectrometric analysis of the pitch dust for PAH revealed 1.2 wt% anthracene/phenanthrene and 1.2 wt% fluoranthene. Other major components were pyrene, chrysene/benz(a)anthracene, benzo(k)fluoranthene and benzo(a)pyrene/benzo(e)pyrene. Minor components included acenaphthene and dibenzfuran. No alpha-or beta-naphthylamine was detected (Hervin and Emmett, 1976a).

During the laying of a new pitch roof using pitch heated to 190 to 204°C (375 to 400°F), the cyclohexane soluble fraction varied from 0.02 to 0.49 mg/m^3 in personal air samples on 26 workers and from 0.04 to 2.38 mg/m^3 in area samples. The average range of worker exposure to PAH was 0.017 to 0.083 mg/m^3. A bulk sample of pitch used at the job contained 270 ppm BaP/BeP and 4.89 wt%

cyclohexane solubles, of which 1.9 to 13 wt% was PAH. A bulk sample of asphalt contained 10.3 wt% cyclohexane solubles, of which 0.5 to 3.2 wt% was PAH, but no BaP/BeP was detected. Neither sample contained α- or β-naphthylamine (Hervin and Emmett, 1976b). Tests of the carcinogenicity of these samples to mouse skin (Bingham et al., 1977a) are described in Chapter VI.

In both operations, most workers had histories of skin photosensitization. Phototoxic keratoconjunctivitis was common in both white and black workers, and was subjectively associated with sunny days or summer (Hervin and Emmett, 1976a,b; Emmett et al., 1977). It was suggested that eye involvement in roofing workers may be minimized by reducing exposure to pitch volatiles to levels below 0.2 mg cyclohexane solubles/m^3. In dusty operations involving pitch, no signs of conjunctivitis were observed at levels of cyclohexane solubles below 0.11 mg/m^3 (Hervin and Emmett, 1976a).

In a study of mortality in 5939 roofers exposed to asphalt and pitch for at least nine years before 1960 (Hammond et al., 1976; Selikoff, 1976), an increase in lung cancer mortality, expected if inhalation of BaP is a cause, was not observed until the time of exposure reached twenty years (Table V-4). Smoking histories were not obtained. Mask filter BaP levels ranging from "not detectable" to 135 µg/7-hr day were reported for all jobs at the work site, with average exposure levels of 1.4-53 µg BaP/7 hr day (Hammond et al., 1976).

b. Paving:

Although bitumens for paving materials are now generally asphalt, varying amounts of coal tar pitch have been used for this purpose. Cases of clinical symptoms in road workers cannot readily be attributed to coal tar pitch or to asphalt.

TABLE V-4. MORTALITY RATIOS FOR SEVERAL CAUSES OF DEATH IN ROOFERS

Cause of Death	Time in Roofing Union 9-19 yrs.	20+ Yrs.
ALL DEATHS	1.02	1.09
Respiratory*	1.96	1.67
Accidents	1.59	1.41
ALL CANCERS	1.07	1.45
Buccal cavity, pharynx, larynx, esophagus	1.04	1.95
Stomach	0.54	1.67
Bladder	0.82	1.68
Prostate	1.87	1.38
Leukemia	1.67	1.68
Lung	0.92	1.59

*Includes emphysema, chronic bronchitis and asthma.

Source; Hammond *et al.*, 1976

Zorn (1966) reported a case of bladder cancer in a road worker believed to be exposed to pitch but not to other fractions of coal tar. Several brands of paving "tar" were found to contain 0.3 to 3% β-naphthylamine, a known bladder carcinogen, and half as much α-naphthylamine. The concentration of β-naphthylamine was 1.5 to 4 ppm in the air near the tar spraying machine and 20 μg (total) in the worker's long underwear worn for six days without washing.

4. Prevention of occupational disease

Detailed discussions of preventive measures needed to avoid occupational disease from exposure to carcinogenic PAH that may be present in asphalt or coal tar pitch can be found in the criteria document on coke oven emissions (U.S. National Institute for Occupational Safety and Health, 1973), the proposed and final standards on coke oven emissions (U.S. Department of Labor, 1975, 1976), and the criteria documents on asphalt fumes and coal tar products (U.S. National Institute for Occupational Safety and Health, 1977a,b). The following information is based on these references and on Bolton (1976), Ketcham and Norton (1960), Crow et al. (1961), Garrett (1977), and Cheng (1977).

Prevention of any occupational disease can be broadly divided into four areas of concern: education of employer and employee, medical surveillance, protective devices or measures, and personal hygiene practices.

Education:

Fundamental to the prevention of occupational disease is the informed worker. In order to protect himself and others, each worker must recognize hazards in the workplace. A minimal program would involve displaying in a prominent place a clearly, simply written poster with the following information: the generic names of substances to which workers are exposed, including not only materials being handled, but major by-products that may be present; possible routes of exposure; acute or chronic symptoms of diseases that may result from exposure; and personal measures the worker can take to minimize exposure.

Medical Surveillance:

The surveillance program can include an educational program. Workers can receive more detailed information on possible job-related difficulties as well as information on avoiding occupational disease. This may include discussion of the role of smoking and use of alcohol in predisposing workers to certain conditions.

It has been suggested that the preplacement physical examination for workers who will potentially be exposed to "coal tar pitch volatiles" include the following: a complete medical history; tests of pulmonary function, including forced vital capacity; chest X rays; sputum and urine cytologies; urinalysis; blood count; and a complete skin examination, noting suspicious lesions on a permanent record, ideally with photographs. Workers should have annual physical examinations, with semi-annual checkups after age 45 or after ten years of employment.

Protective devices or measures:

Engineering controls should be installed to eliminate exposure. Until this is accomplished, or during situations involving high exposures, respirators approved by NIOSH or the Mining Enforcement and Safety Administration should be worn.

Barrier creams may be helpful in avoiding skin contact, although there is controversy as to their efficacy. Workers exposed to sunlight and pitch fumes should use a topical sunscreen, Five percent para-aminobenzoic acid (PABA) in alcohol is recommended.

Goggles and garments which minimize skin contact with dust or volatiles should be worn. Disposable clothing may be used.

Clothing that had been contaminated by pitch fumes during normal work was found (Masek et al., 1972; Kandus et al., 1972) to contain 11.55 µg BaP/g (average), while underwear contained an average of 5.47 µg BaP/g. PAH, as indicated by BaP, accumulated in work clothing in spite of repeated washings. For example, clothing laundered after every two work shifts contained an average of 0.41 µg BaP/g clothing after two weeks, 0.86 µg BaP/g after three months, and 3.15 µg/g after twelve months. Therefore, in addition to frequent and thorough cleaning, garments should be replaced often.

It has been suggested that employers supply, launder and frequently replace all work clothing, including boots and underwear. In this way, clothing contaminated with potentially carcinogenic PAH can be handled by supervised laundry personnel with adequate control of exposure, emissions from dry cleaning, or effluents from laundering.

Personal hygiene:

After normal work, before doing anything else, hands should be washed. After contaminations and after every work shift, workers should shower thoroughly.

The use of waterless cleaners followed by soap and water has been recommended.

"Black light" (long wave ultraviolet) has been used for checking workers after washing to detect any unremoved fluorescence. It is still recommended by some (Bolton, 1976), but there is controversy over the benefit of regular exposure of workers to a potential carcinogen or cocarcinogen for the purpose of detecting other potential carcinogens.

C. Effects of Experimental Exposure to Coal Tar Pitch

The first experimental evidence that coal tar pitch is a photosensitizing agent was presented by Foerster and Schwartz (1939). Patch tests on the skin of pitch workers and controls under various physiological conditions using pitch in a variety of solvents showed that in most subjects pitch elicits phototoxic reactions to light with wave length from 390 to 500 nm. No reactions were seen to ultraviolet (UV) light less than 250 nm or to infrared light. Sunlight filtered through window glass did elicit a phototoxic response. Patch areas which were washed before irradiation still showed typical pitch photosensitization.

Crow et al. (1961) patch tested workers with pitch dissolved in chloroform. Most subjects complained of "pitch smarts" when exposed to light from 340 to 430 nm. The erythematous response in these workers was similar to pitch phototoxicity seen in the field. The reactivity of a patch-tested area, however, remained for several weeks rather than several days.

Individual components of pitch have been tested for their photosensitizing properties. Foerster and Schwartz (1939) reported phototoxic responses to anthracene (strongest), acridine and phenanthrene, but stated that none of these compounds alone was responsible for the phototoxicity of pitch. Crow et al. (1961) found that anthracene, but not acridine, regularly caused phototoxic reactions in patch tests with light from 340 to 380 nm. Kaidbey and Kligman (1977) reported that anthracene, fluoranthene and phenanthrene are as phototoxic as coal tar.

D. Effects of Experimental and Therapeutic Exposure to Coal Tar Medications

Crude coal tar preparations, long claimed to have useful antipruritic, antiacanthotic, vasoconstrictive, keratoplastic and antiparasitic properties (Obermayer and Becker, 1935), are among the most commonly used dermatological medications for the treatment of psoriasis, eczema, and other chronic skin diseases (Gruber et al., 1970). Such medications, with various trade names, are formulated from crude (unfractionated) coal tar, which does not fall within the scope of this report. Biological effects of crude coal tar medications are included here because the properties related to their effectiveness (photosensitization) and side effects (cancer) appear to be attributable to their content (30 to 60%) of coal tar pitch.

When tested by continuous occlusive application to the backs of young adult males for three weeks, 25% crude coal tar and undiluted coal tar distillate were equally acnegenic (Kaidbey and Kligman, 1974a). The lower boiling fractions of coal tar seemed to be irritating, whereas the higher boiling fractions, with keratoplastic properties, were most effective therapeutically (Obermayer and Becker, 1935). When application as a 5% mixture in hydrophilic ointment to forearms of young adults was followed by exposure to long ultraviolet light (UVA), crude tars were more phototoxic than partially refined tars or liquor carbonis detergens.

According to Kaidbey and Kligman (1977), the antipsoriatic potential of a tar parallels its phototoxicity, crude coal tars being more effective than fractions thereof.

There is controversy about both the effectiveness and the safety of the combined use of coal tar and ultraviolet light in treatment of psoriasis.

Marsico and Eaglstein (1973) reported that crude coal tar and short-wave ultraviolet light are more effective against psoriasis when administered consecutively than when used separately. Young (1972) found that ultraviolet and coal tar together produced no beneficial effect that tar alone could not have conferred. He stated, however, that varying the concentration of coal tar used with UV light may change the outcome of tar-UV experiments on psoriatic patients.

Coal tar and coal tar preparations have been tested for phototoxicity and photoaugmentation, without regard for antipsoriatic potential. Crow _et al_. (1961) saw no photosensitization using crude coal tar and light. Liquor picis carbonis, a standard refined tar preparation, caused phototoxic effects at 340-380 nm in most subjects tested. Everett and Miller (1961) tested tars derived from anthracite coal and bituminous coal and reported that the photosensitization reaction depends not on the source of the tar, but on exposure to light of wavelenth 350-400 nm.

Zesch (1972) reported that subjects had photosensitization reactions following tar baths and exposure to light from 340-360 nm. In order to determine how deeply the tar preparations penetrated, he examined excised human skin painted with several standard tar preparations. Fluorescence was observed in the horny layer of skin.

Kaidbey and Kligman (1975) reported that photoaugmentation may be an aspect of photosensitization. UVA (long ultraviolet) and UVB (280-320 nm) administered in any order within a six hour interval will produce sunburn in smaller doses than either administered alone. Application of coal tar followed by irradiation with UVA, then UVB, augmented the phototoxic reaction to coal tar in the majority of subjects. Damage at the microscopic level was more pronounced with coal tar and UVA plus UVB than with coal tar and UVA alone.

Crow et al. (1961) and Kaidbey and Kligman (1977) reported that the phototoxic response was eliminated by curtailment of the blood supply to the area patch tested with coal tar or anthracene for several minutes prior to and during irradiation. This result suggests that the photosensitization reaction, at least in the case of coal tar and derivatives, is oxygen dependent.

The photosensitizing capacity of crude coal tar was found to be related to the penetrating ability of the vehicle, being highest in emulsion-type vehicles, such as hydrophilic ointment, and almost abolished in lanolin or polyethylene glycol (Carbowax) (Kaidbey and Kligman, 1974b).

However, Suhonen (1976) reported a well-defined long lasting phototoxic response when five percent coal tar was applied in a Carbowax base and occluded for 24 hours.

Coal tar has repeatedly produced skin cancer in animal experiments (see Chapter VI). Workers exposed to coal tar and pitch have an increased risk of skin cancer. Even so, no epidemiological studies have indicted the therapeutic use of coal tar. Swanbeck (1971) found that the frequency of psoriasis and eczema (two conditions of epidermal hyperplasia commonly treated with coal tar) is the same in populations with squamous cell carcinomas as in noncancer populations. He also noted that squamous cell carcinomas sometimes develop at scar sites, and suggested that epidermal hyperplasia of psoriasis and eczema, in contrast to the epidermal atrophy of scars, may not predispose a site to cancer.

An international survey indicated that dermatologists have very strong clinical impressions that cancer of the skin is not a problem in patients treated with coal tar preparations. A psoriasis questionaire suggested that coal tar does not cause an unduly high incidence of skin cancer among users, although some cancers were seen in patients who used coal tar medications in combination with X-ray or other treatment (Skin and Allergy News, 1977).

Only a very few case histories of skin cancer possibly related to use of coal tar medications have appeared in the literature. Rook et al. (1956) referred to five patients who allegedly developed cancer after application of coal tar medications. He described the case of a sixty-year-old road worker with no history of tar contamination who developed two squamous cell carcinomas on his thigh after treating the area for 34 years with various tar ointments, using about one ounce of tar preparation every two weeks. Greither et al. (1967) reviewed thirteen previously published cases of human skin cancer following prolonged application of therapeutic tar preparations (not all coal tar), including the cases cited by Rook et al. (1956).

Recently, Zackheim (1978) commented on the earlier reviews and indicated the need for long term animal tests with tar products in various bases. While he considered tar preparations to be effective and reasonably safe dermatological medications, he protested over-the-counter availability of these products for prolonged self-medication.

VI. BIOLOGICAL EFFECTS ON ANIMALS AND PLANTS

A. Effects on mammals and birds.

1. Poisonings:

In addition to the toxic effects of bituminous materials observed in exposed humans, cases of poisoning have been reported in animals accidentally exposed to coal tar pitch and other coal tar products, but not to asphalt.

A number of cases of coal tar poisoning in swine were reviewed by Kernkamp (1964), who considered the disease an acute one, often fatal, with liver lesions as the most important indication. One source of exposure to coal tar pitch was fragments of clay pigeons (made from powdered limestone and coal tar pitch) deposited as long as 35 years earlier when the area was used as a target range. Other sources included various materials coated or joined with pitch, such as tarred pipelines, stone chips, and roofing paper.

Maclean (1969) described severe chronic effects on the growth rate and on Vitamin A utilization by sows and new-born piglets, including some deaths with hepatitis. The disease was attributed to unidentified components of coal tar pitch used as a joint filler for concrete slab housing and as a coating on granite chips for road use.

Lambers and Van Ulsen (1973) reported that 30 pigs developed ascites (accumulation of serous fluid in the abdomen) as a result of chronic coal tar pitch poisoning from pulverized briquettes placed in their sties by the owner. Autopsy of one of the pigs revealed the enlarged mottled liver typical of pitch poisoning.

2. Toxicity:

Studies of toxic effects have been reported for coal tar and pitch, but not for asphalt.

a. Coal tar and pitch

Young pigs (4 to 9 weeks old) fed powdered clay pigeon targets for up to two weeks developed severe hepatic centrilobular necrosis and hemorrhage, often fatal, with related hematologic changes (Libke and Davis, 1967; Davis and Libke, 1968). Clay pigeon material administered to goats in large doses (total 675 to 1350 g) by stomach tube during a three week period was not fatal, but produced non-hemorrhagic hepatic lesions and weight loss in all animals (Libke and Davis, 1968). All levels of ground clay pigeons fed to Pekin ducklings were found to be acutely toxic, with depressed growth and dose-related gross abnormalities, chiefly edema, and characteristic microscopic liver changes (Carlton, 1966).

The toxicity of a pitch-tar varnish containing no benzo(a)pyrene was studied by Kudrin et al. (1968). The varnish, of unspecified source and composition, was used for the waterproofing of logs to be transported by floating in rivers and reservoirs used as sources of drinking water. White mice receiving pitch-tar varnish daily for ten days in oral doses of 100 mg/kg showed a decrease in weight gain with inconclusive effects on behavior (toleration of load burden). In three-month studies, white rats receiving the varnish in daily oral doses of 10 mg/kg or of 1 ml of an aqueous solution containing 100 mg/l showed no changes in behavior, nervous system function, blood chemistries, and general condition. The group exposed to 10 mg/kg showed significantly decreased weight gain starting in the second month, and pathological changes in several organs (not identified). The varnish was considered harmless at a concentration of 5 mg/l, with a maximum permissible limit of 10 mg/l.

Bokov et al. (1974) exposed male Wistar rats 24 hours per day for 90 to 150 days to air containing material volatilized at 40 to 50°C (104 to 122°F) from UKhM-N bitumen mastic (an asphaltic bitumen). Xylene (0.04 mg/m^3) was identified in the chamber air, while phenol and unsaturated hydrocarbons were expected but not found. Bone marrow cells of the exposed animals showed an increase in chromosome aberrations at the late anaphase-early telophase stage, with an increased number of fragments and a decreased number of chromosome bridges.

Kovalenko (1965) found that injection of bituminous coal pitch into the surgically exposed preputial sebaceous glands of male rats produced inflammatory epithelial proliferation, with metaplasia to stratified squamous epithelium.

Although the phototoxicity of coal tar pitch affects a large proportion of exposed workers (see Chapter V), almost no studies have been conducted in experimental animals. Skin painting studies have been directed primarily to the investigation of carcinogenicity. Emmett et al. (1977) studied the effect on rabbit eyes of roofing coal tar pitch volatiles prepared by collecting vapors from a large sample maintained at 200°C. Instillation of 10 μl of this distillate into the conjunctivae of rabbits maintained in UV-free quarters produced only minimal or mild temporary irritation. Irradiation with long-UV light (330-380 nm) at 2.0×10^2 joules/m^2 shortly after conjunctival instillation produced marked photophobia and severe keratoconjunctivitis.

Phenolic compounds are often present in high concentrations in coal tar fractions (anthracene oil, creosote oil) boiling below coal tar pitch. Such fractions are toxic and may cause high mortality when administered repeatedly, as in some studies of carcinogenicity described below. Some phenols may act as cocarcinogens (Boutwell and Bosch, 1959; Tye and Stemmer, 1967). Phenols are present in only small amounts in hard pitch, but may occur in toxic concentrations in heavy tars or soft pitches which contain considerable amounts of lower boiling material. Grigor'ev (1954, 1959) found that heavy tars from Cheremkhovo coal, thinned with 30% benzene, produced high mortality in mice when applied to the skin three times per week for six months. The severity of the toxic reaction (degenerative changes in internal organs including liver, spleen, and kidney) was related to the phenolic content (20 to 34%), and interfered with possible development of skin tumors (Table VI-1). Likewise, anthracene oil (lower boiling than coal tar pitch) and its chromatographic fractions were found by Domagalina (1954) to be highly toxic when applied to the skin of mice twice weekly for 16 to 45 weeks (Table VI-1).

b. Coal tar medications:

Although crude coal tar ointments have been widely used for the treatment of hyperplastic epidermal disease such as psoriasis, few experimental studies have been performed to evaluate their side effects or to elucidate their mode of action.

Stone and Willis (1969) found that application to rabbit skin of coal tar USP (crude coal tar) as a 5% mixture with a hydrophilic ointment increased the severity of experimentally produced bacterial infection. When 5% crude coal tar mixed with a triple antibiotic ointment was applied to experimentally produced wounds of rabbit ears, there was a 46% delay in wound healing, with marked follicular hyperkeratosis around the wound (Stone and Anthony, 1970).

Application of crude coal tar fractions with boiling ranges either below or above 250°C at 15 mm Hg produced acanthotic changes (thickening of the prickle-cell layer) in guinea pig skin. The acanthotic activity of the fraction boiling up to 250°C at 15 mm Hg appeared to reside chiefly in the neutral portion, which also produced moderate inflammation (Schaaf, 1957).

In studies of the effects of locally applied therapeutic agents upon epidermal protein and nucleic acid synthesis, application of crude coal tar (15% in cottonseed oil) to guinea pig skin three times per day for four days caused inhibition of epidermal amino acid incorporation (Freedberg, 1965).

Crude coal tar (6% in petrolatum) and a refined coal tar preparation (Estar gel, 0.5% crude coal tar) were found to depress DNA synthesis in vivo in normal and proliferating skin of the hairless mouse. The effect was greatly increased when the tar was applied in combination with near ultraviolet light (UVA, 320-400 nm) (Stoughton et al., 1978).

3. Carcinogenicity:

Investigations of the chronic effects of asphalt and pitch samples have been concerned chiefly with carcinogenicity. Studies of exposure by skin painting, injection, and inhalation are summarized in Tables VI-1, VI-2, and VI-3, respectively. These tables include pertinent quantitative data (dosage, duration, number of animals, tumor incidence, etc.) from the original articles. The information in the tables is mentioned in the text under the appropriate materials, but is arranged in the tables, and referred to in the text, by author and year to simplify identification of the substance studied. Where both asphalt and coal tar samples were included in the same study, data are presented together in the tables to permit ready comparison of results obtained under the same test conditions.

a. Introduction:

Because of their viscous nature, many asphalt or pitch samples must be warmed or diluted with a solvent to permit satisfactory skin application or injection. The results of such tests may be influenced by inadequate contact of "solid" samples with tissues or by cocarcinogenic or inhibitory effects of solvents.

If the dosage and/or frequency of application is too high, the toxicity of components of the sample (or the solvent) may produce high mortality before tumors can develop or may alter the pattern of tumor incidence by interfering with normal growth.

TABLE VI-1. CARCINOGENICITY OF ASPHALTS, TARS, AND PITCHES APPLIED TO THE SKIN

Material	% BaP	Species	Original number of animals	Concentration vehicle	Dosage	Frequency	Duration	Number of skin tumors	Reference
Asphalt[a]		mice (C57 black)	68	in benzene		2x/wk		12 carcinomas	Simmers et al., 1959
" air refined[b]		"	50	heated	75-100 mg	1-3x/wk	2 yr	1 papilloma	Simmers, 1965a
"		"	20	+9% toluene	20-30 mg	3x/wk	2 yr	9 carcinomas	"
" steam refined[b]		"	63	heated	75-100 mg	3x/wk	1½ yr	3 carcinomas + 2 papillomas	"
" saturates & aromatics[c]		"	50		33 mg	3x/wk	1½ yr	13 carcinomas + 13 papillomas	Simmers, 1965b
Asphalt[d]		"		in acetone		2x/wk	lifetime	no cancers	Hueper, 1965
Road asphalts[e]		"	250	in acetone	1 drop	2x/wk	2 yr	1 carcinoma + 2 papillomas	Hueper & Payne, 1960
"		rabbits		heated	1 drop	2x/wk	2 yr		
Roofing asphalt		mice	50	"		2x/wk	2 yr		"
		rabbits	6	"		2x/wk	2 yr	no cancers	"
Coal tar		mice (C57 black)	50	"		"	"		"
Coal tar fume condensate[f]		mice	50	1:3 in olive oil				22 carcinomas + 4 papillomas	"
Asphalts, road paving (8)		mice (Swiss)	218	10% in benzene	25 µl	2x/wk		1 carcinoma + 5 papillomas	Wallcave et al., 1971
Coal tar pitch, roofing (2)		"	58	9% in benzene (filtered)	"	"		31 carcinomas + 53 papillomas	"
Asphalts, straight run (3)		mice (SS-57) white	177	40% in benzene		1x/wk	19 mo	5 tumors	Kireeva, 1968
Asphalts, cracked (2)		"	99	"		"	"	13 tumors	"

(cont'd)

TABLE VI-1. CARCINOGENICITY OF ASPHALTS, TARS, AND PITCHES APPLIED TO THE SKIN (cont'd)

Materials	% BaP	Species	Original number of animals	Concentration vehicle	Dosage	Frequency	Duration	Number of skin tumors	Reference
Coal tar pitch		mice (SS-57) white	49	40% in benzene		1x/wk	19 mo	29 carcinomas + 8 papillomas (at 12 mo)	Kireeva, 1968
Asphalt, straight run	∼0	mice (C3H)	30	50% in triacetin	50 mg	2x/wk	79 wk	1 benign	Bingham and Feasley, 1972
Asphalt, thermal	0.08	"	30	"	"	"	85 wk	7 malignant + 4 benign	"
Coal tar pitch	0.59	"	30	"	"	"	41 wk	27 malignant	"
Raw coal tar pitch	0.62%	"	20	50% in toluene	50 mg	2x/wk	32 wk	14 " (100%)	Bingham and Barkley, 1976
Roofing pitch (coal tar)	0.064	"	50	"	50 mg	2x/wk		45 carcinomas + 3 papillomas	Bingham et al., 1977a
Roofing bitumen	0.072	"	50	"	"	"		39 " + 8 "	"
Roofing pitch (asphalt)	<0.0004	"	50	"	"	"		no tumors at 49 wk	"
Coal tar[g]	0.67%	"	30		50 mg	2x/wk	32 wk	28 malignant + 2 benign	Bingham, 1975
Coal tar from by product coke oven[h]	0.74%	mice C3H			50 mg	2x/wk		100% tumors (82% malignant)	Horton et al., 1963
Coal tar pitch from Silesian coals		mice	48	1:1 in benzene		2x/wk	22 wk	14	Gorski, 1959
", hard		"	21	"		"	"	8	"
", soft		"	28	"		"	"	14	"
Pitch condensate (70% tar)[i]		"	26	20% in benzene		1x/wk		15	Gorski & Malchar, 1965
" deposits on snow[i]		"						5	

(cont'd)

TABLE VI-1. CARCINOGENICITY OF ASPHALTS, TARS, AND PITCHES APPLIED TO THE SKIN (cont'd)

Material	% BaP	Species	Original number of animals	Concentration vehicle	Dosage	Frequency	Duration	Number of skin tumors	Reference
Heavy tars from Cheremkhovo coal[j]	0	mice (white)	174			3x/wk	6 mos	2 cancers + papillomas (high mortality)	Grigor'ev, 1954
" [k]	0.01%	"	64	30% in benzene		"	"	no tumors in 19 mo. (high mortality)	Grigor'ev, 1959
Coal tar chromatographic fractions									
Pre-BaP		mice	20				16 wk	0	Berenblum & Schoental, 1947
"		rabbits	5				"	4	
BaP		mice	20				"	10	
"		rabbits	5				"	3	
post-BaP (combined results)		mice	60				"	5	
		rabbits	15				"	8	
Anthracene oil		mice	10			2x/wk	39 wk	1 tumor (high mortality)	Domagalina, 1954
" Pre-BaP	0	"	21			"	28-41 wk	8 tumors out of 11 surviving mice	
" other fractions		"	25			"	16-45 wk	2 tumors (high mortality)	

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[a] from Western U.S. crudes - pooled 3 steam and 3 air-refined
[b] 3 pooled from Western U.S. crudes - not the same as [a]
[c] pooled saturates and aromatics from 3 steam refined Western U.S. crudes
[d] native, straight run, air blown
[e] from 4 crudes
[f] condensed from coal tar vaporized at 250-275°F (121-135°C).
[g] sample same as Bingham et al., 1977b, and MacEwen, 1976 (inhalation)
[h] sample same as for inhalation
[i] benzene extract
[j] 20-34% phenols
[k] 27% phenols

TABLE VI-2. CARCINOGENICITY OF INJECTED ASPHALT AND COAL TAR SAMPLES

Material	Species	Route	Concentration/ Vehicle	Dosage	Frequency	Duration	Original Number of Animals	Number of Sarcomas	Reference
Asphalt from Western US crudes pooled: 3 steam-refined +3 air-refined[a]	mice (C57 black)	sc	1% in olive oil	0.2 ml	2 x/wk then 1 x/wk	41 wk	33M, 29F	8	Simmers *et al.*, 1959
Asphalt from Western US crudes pooled: 3 air-refined[b]	"	sc	heated	200 mg	single dose repeated after 4 mo		25M, 25F	3	Simmers, 1965a
Asphalt from Western US crudes pooled 3 steam-refined[b]	"	sc	heated	200 mg	single dose repeated after 3 mos, 9 days		25M, 25F	0	"
Steam-refined asphalt from California crude, pooled saturates and aromatics	"	sc		0.5 ml	single dose		20M, 27F	8	Simmers, 1966
"	"	sc		0.25 ml	every other week	8 injections	26M, 23F	7	"
"	"	sc		1 ml	less than weekly	≤11 injections	12M, 16F	7	"
Road asphalts from 4 crudes[c]	"	im	50% in tricaprylin	0.1 ml	biweekly	6 doses	200	3	"
"	rats (Bethesda black)	im	50% in tricaprylin	0.2 ml	biweekly	12 doses	120	13	Hueper and Payne, 1960
Coal tar fume condensate	mice (C57 black)	im	1:3 in olive oil	0.15 ml	"	6 doses	100	50	"

[a] Sample same as in Simmers, 1964

[b] Sample not the same as in Simmers, 1959

[c] Results combined from separate tests

TABLE VI-3. CARCINOGENICITY OF INHALED ASPHALT AND COAL TAR SAMPLES

Material	Species	How tested	Concentration	Frequency	Duration	Original no. of animals	Tumors	Reference
Asphalt from Western US crudes, pooled: 3 steam-refined +3 air-refined^{a}	mice (C57 black)	aerosol in moist air^{b}		30 min/day 5 days/wk	16½ mo	20	1 papillary adenoma^{d}	Simmers, 1964
	"	smoke from sample heated at 250°F^{c}		6-7½ hr/day 5 days/wk	21 mo	30	1 bronchial adenoma^{d}	"
Roofing asphalt air blown, flash point 392°F	guinea pigs rats (Bethesda black)	vaporized at 250-275°F		5 hr/day 4 days/wk	2 yr	30 65	no cancers of skin or lungs "	Hueper & Payne, 1960
Coal tar	guinea pigs rats	"		"	"	42 75	" "	"
Coal tar^{e}	mice (C3H)	vaporized at 800°C	0.30 mg/l	2 hr/day 3 days/wk	35 wk	33	5 squamous cell tumors (lung) (1 carcinoma)	Horton et al., 1963
Coal tar^{f}	"	"	0.20 mg/l (8 wk) then 0.12 mg/l	"	55 wk	100	4 adenocarcinoma 19 intrabronchial adenoma 10 squamous metaplasia	Tye & Stemmer, 1967
", non-phenolic fraction	"	"	"	"	"	50	11 intrabronchial adenoma 2 squamous metaplasia	"
Coal tar^{g}	hamsters	tar-coated coal dust	65 mg/m^{3}	6 hr/day 3 days/wk	14 mo	23	lung (4 benign) skin (1 fibrosarcoma)	Bingham et al., 1977b.
"	"	" + n-dodecane	" 600 mg/m^{3}	"	"	38	lung (4 malig., 2 benign) liver (2 malig., 4 benign)	"
Coal tar^{h}	rabbits hamsters rats mice ICR-CF-1	aerosol	20 mg/m^{3} ^{i}	continous	90 days	24 100 164 75	some skin no skin 10 skin incl. squamous cell carcinomas + 30 lung incl. alveolargenic carcinomas	MacEwen, 1976
	" JAX-CAF					75	10 skin + 6 lung	

(cont'd.)

TABLE VI-3. CARCINOGENICITY OF INHALED ASPHALT AND COAL TAR SAMPLES (Cont'd)

Materials	Species	How tested	Concentration	Frequency	Duration	Original no. of animals	Tumors	Reference
Coal tar + 20%BTX[j]	mice ICR-CF-1	aerosol	10 mg/m^{3k}	Continuous	90 days	225	44 skin + lung incl alveolargenic carcinoma	MacEwen, 1976
	" JAX-CAF-1							
	hamsters					75	18 skin	
	rabbits						1 skin	
	rats					14		
						80		
Coal tar + 20%BTX[j]	mice ICR-CF-1	"	10 mg/m^3	6 hr/day 5 days/wk	18 mos (incomplete)	75		
	" JAX-CAF-1							
	monkeys					50	no skin tumors during 1st 8 mos.	"
	rabbits					14		
	rats					18		
						80		
Tarry fumes from combustion of anodes of Al electrolysis	mice C3H	vaporized at 400°C	BaP content 1.4 µg/1 (0.2-3.4)	continuous	11 mos	144	skin neoplasms	Mestitzova, 1961
	" A				10 mos	99	lung metaplasia of respiratory epithelium (nodules at 5 mo → neoplasms)	
Road dust from tarred roads (2% tar)	mice	dust cloud (1-2 mg tar/day)		4-6x/day 5 days/wk	1 year	73	39 skin cancers + 7 skin warts 45 lung tumors	Campbell, 1934
	guinea pigs					22	incomplete	
	rabbits					4	incomplete	

[a] sample same as Simmers, 1959
[b] inhalation only
[c] inhalation with exposure of skin and food
[d] not malignant
[e] 0.74% BaP; 4.5% phenols
[f] sample same as Horton, 1963
[g] 0.67% BaP; sample same as MacEwen, 1976 (without BTX)
[h] 0.67% BaP; sample same as Bingham et al., 1977b
[i] also tested at 10, 2, and 0.2 mg/m^3
[j] Benzene - Toluene - Xylene
[k] also tested at 2 and 0.2 mg/m^3

Fogs or fumes for inhalation may be produced by various procedures involving heating to a wide range of temperatures which may influence the composition of the fumes. The failure of inhaled materials to produce malignant tumors of the lung may be related to lack of susceptibility of the test species under the specific conditions of exposure used, since coal tar samples known to be highly carcinogenic to the skin have not always produced lung tumors in inhalation studies (Saffiotti, 1969).

Injections by subcutaneous, intramuscular, or intraperitoneal routes are of doubtful significance because they do not represent a normal route of human exposure, Tumors at injection sites have been attributed by some investigators (Hueper and Payne, 1960) to carcinogenic components of the samples but by others (Shubik et al., 1962) to physical effects which are unrelated to the composition of the material injected.

All of these factors may modify the carcinogenic potential of the samples so that accurate evaluation is difficult. Comparison is further complicated by use of various species and strains of animals differing in susceptibility and in spontaneous incidence of tumors.

The extensive surfaces paved with asphalt and tar and the processes used for their construction have been regarded (Hueper and Payne, 1960; Hueper, 1963) as potential sources of air emissions and surface run-off water pollutants which may be harmful to human health, particularly as possible causes of cancer. The composition of such potential environmental contaminants under conditions of use has been discussed in Chapter II.

In an early study, Campbell (1934) exposed mice, guinea pigs, and rabbits intermittently to clouds of a dust collected from tarred roads (Table VI-3). The dust, containing about 2% of "tar", produced malignant skin tumors in 45 to 70% of the surviving mice and an increased incidence (59 to 80%) of lung tumors, including some malignancies. In spite of such early concern, few studies of bituminous materials have been carried out in experimental animals.

b. Asphalt:

Hueper and Payne (1960) applied road asphalts derived from four American crudes (Venezuela, Mississippi, Oklahoma, and California) to mice by skin painting (Table VI-1) and to mice and rats by intramuscular injection (Table VI-2). Skin application to a total of 250 mice produced only 2 carcinomas and 2 papillomas. A petroleum roofing asphalt likewise produced only 1 questionable carcinoma in 50 mice. Inhalation of fumes from this material produced no lung tumors in 65 rats (Table VI-3). In a later study (Hueper, 1965), no cancers were produced in mice by skin application of straight-run petroleum asphalt, air-blown asphalt, or natural Trinidad asphalt (Table VI-1). The results indicated to the authors that asphalts do contain carcinogenic materials but that their potency may be reduced by air-blowing or by dilution with natural asphalts.

A roofing pitch (petroleum asphalt) tested by Bingham et al. (1977a) produced no skin tumors in 50 mice when applied to the skin as a 50% mixture with toluene (Table VI-1).

Simmers and co-workers investigated the carcinogenicity to mice of a series of asphalt samples prepared from Western U.S. crudes at California refineries (Simmers et al., 1959; Simmers, 1964, 1965a,b, 1966). Although dilution was sometimes necessary to produce adequate skin contact, some carcinomas resulted from skin painting (Table VI-1) of separate or pooled samples of air- and steam-refined asphalts or of the pooled aromatic and saturate fractions from steam-refined asphalt, which were believed to retain all of the potential carcinogenic agents. The pooled sample from air-blown and steam-blown asphalts, which had produced skin cancer, caused no respiratory cancers when inhaled by mice (Table VI-3), although other changes in the lungs were observed.

Wallcave et al. (1971) also studied the carcinogenicity of asphalt samples. Eight road paving grade straight-run asphalts, not air-blown, from U.S., South American, and Mid-East crudes produced only one carcinoma and five papillomas when applied to the skin of a total of 218 mice (Table VI-1). These asphalts were found to contain small amounts of most of 17 PAH (some carcinogenic) which were found in higher quantities in two coal tar pitch samples which produced skin tumors in over 90% of treated mice (Table VI-1).

A straight-run asphalt applied to the skin of mice by Bingham and Feasley (1972) produced only one papilloma in 30 mice, while a thermal asphalt produced seven malignant and four benign tumors in 30 mice. In contrast, coal tar pitch tested under the same conditions (50% in triacetin) produced 27 malignancies in 30 mice (Table VI-1).

Kireeva (1968) found that three straight-run asphalts (40% in benzene) produced only five skin tumors in a total of 177 mice. Under the same conditions, two cracked asphalts produced a total of 13 skin tumors in 99 mice, while coal tar pitch produced 37 tumors (29 malignant) in 49 mice (Table VI-1).

c. Tars and pitches derived from coal

(1) Coal tar:

The first example of experimental carcinogenesis was the production of cancers at the site of painting of coal tar on the skin of rabbits (Yamagiwa and Ichikawa, 1915, 1918) and mice (Tsutsui, 1918). The early isolation of the carcinogen BaP from coal tar pitch by Cook et al. (1933) led to the association of BaP content with carcinogenic activity. Although this association is still widely assumed, it is clear that other compounds contribute to the potency of coal tar. Separation techniques used by

Berenblum and Schoental (1947) produced several fractions which were free of BaP but were found to be carcinogenic to the skins of rabbits and mice (Table VI-1).

Biological studies often mention the use of "coal tar" without any description of source, physical properties, or chemical composition. Confusion in the terminology applied to coal tars and pitches makes comparison of such studies difficult. It is clear, however, that many "coal tar" and coal tar pitch samples are strongly carcinogenic, producing malignant tumors of mouse skin in a large proportion of the test animals within a relatively short time. This activity contrasts sharply with the low incidence and long latent period of tumors from asphalt.

Coke oven coal tar was found by Hueper and Payne (1960) to be carcinogenic when applied to the skin of mice and rabbits (Table VI-1). Fumes produced at 250 to 275°F produced no tumors of the skin or lungs when inhaled for two years by guinea pigs and rats (Table VI-3), but condensate from the fumes produced 26 tumors (22 malignant) when applied to the skin of 50 mice (Table VI-1).

Horton et al. (1963) studied another coal tar sample, obtained from an American by-product coke oven, which contained 0.74% BaP and produced 100% incidence of tumors (82% malignant) within 16 weeks when applied to the skin of mice (Table VI-1). Inhalation by mice for 35 weeks of an aerosol generated from this tar at 800°C produced at least one squamous-cell tumor of the lung (Table VI-3). Similar inhalation techniques were applied by Tye and Stemmer (1967) to phenolic and nonphenolic fractions from this and another coal tar. Incidence in the lungs and trachea of squamous metaplasia, adenomas, and adenocarcinomas appeared to be related to combined exposure to phenols and PAH (Table VI-3).

A coal tar condensate, from which only the low-boiling benzene-toluene-xylene (BTX) fraction had been removed, contained 0.67% BaP and was found by

Bingham (1975) to produce 100% incidence of skin tumors in mice (Table VI-1). A comparison of the potencies to mouse skin of this tar and its dilutions with the potencies of the same concentrations of BaP indicated that the carcinogenicity of this tar could not be attributed entirely to its content of BaP. Inhalation of aerosols produced from the same tar, with or without the BTX fractions, was studied extensively in various species by MacEwen (1976) (Table VI-3). Aerosol particle sizes were determined. Measurement of fluorescent material extracted from tissues was used as an indication of retention of inhaled PAH at various exposure levels. Malignant skin tumors were produced in mice and rabbits, to a limited extent in rats, and not in hamsters.

Inhalation by hamsters of coal dust coated with the same coal tar was found by Bingham et al. (1977b) to induce a low incidence of neoplasms of the lungs and skin (Table VI-3). Simultaneous exposure to n-dodecane, a known skin cocarcinogen (Horton et al., 1957), enhanced the incidence of tumors, including benign and malignant neoplasms of the lung and liver.

(2) Heavy tars or pitches:

Some heavy tars or pitches produced by the coking of coal contain large amounts of phenols or other toxic materials. Thus Grigor'ev (1954, 1959) found that tars from Cheremkhovo coal caused high mortality which interfered with possible development of skin tumors (Table VI-1).

Gorski (1959) reported that soft pitch and hard pitch from Silesian coals produced more papillomas when applied to the skin of mice than did anthracene oil or foundry pitch. Deposits (70% tar) from the surface of pitch cooler pipes rapidly produced skin cancer in mice, while pitch cooler emissions deposited on a snow surface produced some tumors with longer survival (Gorski and Malchar, 1965) (Table VI-1).

(3) Coal tar pitch:

Wallcave et al. (1971) reported that two roofing-grade coal tar pitches from coke oven production caused epidermal carcinomas and papillomas in over 90% of treated mice when applied topically (Table VI-1). The content of 17 PAH and their alkyl derivatives was determined for these pitches and for asphalt samples which had much lower PAH content and caused only a few tumors. Roofing coal tar pitch with a low BaP content was found by Bingham et al. (1977a) to produce a high incidence of tumors when applied to the skin of mice (Table VI-1). Coal tar pitches for use as electrode binders likewise caused very high incidence of malignant skin tumors in mice (Bingham and Feasley, 1972; Bingham and Barkley, 1976) (Table VI-1).

Although electrode binders represent a major use for coal tar pitches, the biological effects of the emissions from production and use of such electrodes have received little attention. Mestitzova (1961) exposed mice to tarry fumes produced at 400°C from anode material (coke dust plus hard coal tar) used for aluminum electrolysis. Measurement of fluorescence indicated that PAH were readily eliminated from lungs and blood but tended to accumulate in the lungs during continuous exposure. Skin neoplasms were produced as well as metaplasia of the respiratory epithelium (Table VI-3).

The use of coal tar pitch as a binder for coal briquettes has also caused concern. Kireeva (1968) found that a coal tar pitch used for this purpose produced 37 tumors (29 malignant) when applied to the skin of 49 mice (Table VI-1). In order to reduce occupational and environmental exposure to this hazard, it was suggested by Kireeva and Yanysheva (1972) that the pitch binder be replaced by straight run or cracked asphalts of low carcinogenicity or that pitch containing briquettes be prebaked before use as fuel.

(4) Coal tar medications:

Pharmaceutical preparations containing coal tar and related tars have been described by Obermayer and Becker (1935). Of these, liantral is a crude coal tar containing all fractions boiling above 80°C (176°F), from which solid carbon has been removed, Liantral (Beiersdorf-Hamburg) No. 429 B with a BaP content of 5 mg/g is used for preparation of the dermatological ointment Locacorten-Tar (Ciba-Geigy brand of flumethasone pivalate) which contains 1.5% tar in a lanolin base, resulting in a BaP content of 0.23 mg/g. This ointment was applied to the skin of 18 hybrid mice five times per week for 1.5 months, then three times per week for 10.5 months for a total of 186 doses containing 4.3 mg BaP within one year. Papillomas, starting at 4 months, developed in 16 mice, with malignant tumors in 13 mice (Linnik, 1970; Shabad et al., 1970).

Another crude coal tar preparation, pix lithanthracis, produced carcinomas of the skin in 54% of a group of 100 female NMRI mice when applied to the skin as a 5% solution in dimethylsulfoxide. Application of two drops three times per week was reduced to one drop once weekly after four weeks because of toxicity; treatments continued for two years. No papillomas or squamous cell carcinonas were produced following similar treatment with a new synthetic tar mixture prepared from very pure coal tar fractions (aromatic hydrocarbon, oxygen, nitrogen, and sulfur compounds), omitting all known carcinogenic and photodynamically active compounds. The synthetic material was as effective therapeutically as the usual coal tar preparation (Hilfrich and Mohr, 1972).

Although coal tar was not included, several other tar-containing skin medications commercially available in Japan were found by Hirohata et al. (1973) to contain BaP and other PAH and to cause cancer when applied to the skin of female CF#1 mice three times per week for up to 630 days.

(5) Other coal-derived tars:

Although coal tar distillates which do not include pitch are not included in the scope of this report, it should be mentioned that some such products may contain carcinogens or components which modify carcinogenic activity. Domagalina (1954) studied anthracene oil containing chromatographic fractions free of BaP which were highly carcinogenic to the skin of mice (Table VI-1). Sall and Shear (1940) and Cabot *et al*. (1940) found that fractions of creosote oil could accelerate (basic fraction) or retard (phenolic fraction) the carcinogenic action of BaP.

As alternative methods of fossil fuel utilization are developed, the carcinogenic potential of tars produced by other coal conversion processes should not be overlooked (Koppenaal and Manahan, 1976). Studies of the carcinogenicity of such materials have been reviewed (TRW Systems and Energy, 1976; Hueper, 1963 Weil and Condra (1960) found that some materials, such as pasting oil, from a pilot plant for a coal hydrogenation process were highly carcinogenic to the skin of mice. The experimental studies of these samples were correlated with observations of the health of workers exposed to the same materials in the pilot plant (Sexton, 1960a,b).

B. Effects on other animals

In spite of the widespread use of asphalt and coal tar pitch in paving, roofing, and underwater coating materials, which offer great opportunity for environmental contamination, their biological effects on species other than laboratory and domestic mammals and birds have received almost no attention.

1. Fish:

Khosa and Chandrasekhar (1972) searched for an inexpensive material to increase fish production by bringing about more rapid development of fish eggs. They found that 50 μg of asphalt in saline injected intramuscularly once weekly for 3 months enhanced maturation of ova and increased vitellogenesis in the teleostean fishes *Clarias batrachus* and *Ophicephalus punctatus*. The increased ovarian activity showed a correlation with changes in the fuchsinophil content of the neurons of the preoptic nuclei. Environmental exposure to asphalt was not considered in the study.

2. Invertebrates:

A freshwater zooplanktonic copepod, *Heliodiaptomus viduus*, was used by Ghosh *et al*. (1974) to evaluate the acute toxicity of the combined effluent of a coal tar mill manufacturing tar and bituminous emulsions. Toxic effects were noted at tar waste concentrations of 0.05% or greater, with 50% mortality at a concentration of 0.243%. It was concluded that the effluent requires adequate treatment or high dilution before discharge.

C. Effects on vegetation:

Damage to vegetation exposed to bituminous emissions has been studied only in areas surrounding European mixing plants for bituminous (asphaltic) road-building materials. Both Knösel and Rademacher (1964) and Kronberger and Halbwachs (1975) found that the vapor and aerosol from the actual bitumen were not harmful to vegetation near the installations.

Kronberger and Halbwachs (1975) investigated the amount of bitumen condensate that would have to be deposited on vegetation to produce harmful effects. Damage to sensitive plants resulted only at experimental levels ≥ 3.2 mg/100 cm^2 of plant surface. Since the maximum level of bitumen vapor condensate detected in the field near 21 Austrian hot-mix asphalt plants was only 0.4-2.0 mg/100 cm^2, it was believed that the level of emissions was too small to cause damage to vegetation near the asphalt plants. Damage actually detected in forests and other vegetation was attributed to SO_2, dust, and soot rather than to the asphaltic bitumen vapors. It was also suggested that dust might protect the plant surfaces.

Knösel and Rademacher (1964) likewise found that vegetation near mixing plants for bituminous road-building materials was not damaged by the vapors and aerosol from the bitumen. In rare cases, sensitive woody plants exposed to the dust and smoke of the drying drum developed some leaf discoloration and necrosis. Field crops and vegetables were not noticeably damaged.

When vapors of tar components were tested on potato leaves, phenazine, xanthene, and 2-methylanthracene were found to be phytotoxic. Acridine, anthracene, fluoranthene, 9-methylanthracene and 9,10-dihydroanthracene were phytotoxic only in the presence of sunlight. Acenaphthene, carbazole, chrysene, fluorene, naphthalene and phenanthrene were nontoxic. Treating the leaves with certain antioxidants (Ziram, Maneb, Dithane M45) eliminated damage by the tar vapors (Halbwachs and Hlawatsch, 1968).

D. Effects on microorganisms:

The degradation of bitumens, asphaltic crude oils, and PAH by microorganisms in soil and water is briefly discussed in Chapter II.

Mutagenesis: The Ames test of mutagenicity to Salmonella typhimurium (Ames et al., 1973) has been utilized to assess the mutagenic potential of some coal tar fractions. Interest in the Ames procedure as a screening test for carcinogenicity is a result of the correlation observed for many materials between mutagenic activity in this test and carcinogenic activity in biological tests using mammals. Wallcave (1975) reported that a small number of mutations occurred with eight chromatographic fractions from coal tar, and that the mutation rate was increased by microsomal activation. Because the total number of mutations produced by polynuclear aromatic hydrocarbons is small compared with the number produced by other classes of compounds such as aromatic amines, Wallcave doubted the adequacy of the S. typhimurium strains for assay of polycyclic hydrocarbons.

E. In vitro studies

Photosensitization of cells by coal tar was studied in Hep-2 cells from human laryngeal carcinoma. At least 1 1/2 hr of contact was required for photosensitization. Firmness of bonding between coal tar and cells increased with length of exposure (Freeman, 1970).

VII. REGULATIONS AND STANDARDS

A. Current Regulations

Several government agencies have established regulations concerning asphalt and coal tar, as set forth in the Code of Federal Regulations (CFR).

1. Environmental Protection Agency

40 CFR 60.11 specifies that new asphalt concrete plants must limit particulate emissions to less than 90 mg/dscm (milligrams per dry standard cubic meter) and less than 20 percent opacity (U.S. Environmental Protection Agency, 1974).

40 CFR 443 establishes effluent limitations for pH, oil and grease, BOD 5, and total suspended solids at new and existing paving and roofing materials (tars and asphalts) point source subcategories: asphalt emulsions, asphalt cement, asphalt roofing, and linoleum and printed asphalt felt (U.S. Environmental Protection Agency, 1975b).

2. Department of Transportation

The Department of Transportation has recognized several names for asphalt, including "asphalt," "road asphalt," "cutback asphalt," and "liquid road tar."

49 CFR 173.115 sets down the definitions of flammable, combustible and pyrophoric liquids. Materials having flash points of 38°C (100°F) or below are classified as flammable liquids, while materials having flash points between 38°C (100°F) and 93°C (200°F) are classified as combustible liquids. In general, all grades of rapid-curing asphalts are considered flammable liquids; most grades of medium- and slow-curing asphalts are combustible liquids. Details on labelling and packaging requirements are specified by law (U.S. Department of Transportation, 1975a).

49 CFR 173.131 (a) (2) provides for continued use of nonspecification cargo tanks equivalent in design to the MC 306 (49 CFR 173.340, 341) required by law for transporting flammable liquids (U.S. Department of Transportation, 1975b).

3. Occupational Health Legislation in Various Countries

[illegible] fourteen industrial nations surveyed, only five had legislation on the manufacture and use of individual carcinogens. Of these five - Ireland, Japan, the United Kingdom, the United States and the USSR - all except the United States also have legislation forbidding the manufacture or importation of specific individual carcinogens (Montesano and Tomatis, 1977). Whether or not specific carcinogens are recognized and regulated by law, many countries nonetheless have workmen's compensation acts for occupationally induced cancers (Table VII-1). There is no national policy in the United States for awarding compensation to victims of occupational cancer, although individual states may allow compensation for work-related disease - which may or may not include cancer. It is estimated that less than five percent of all workmen's compensation awarded is for occupational disease claims (Oil, Chemical and Atomic Workers International Union, 1977).

Standards on asphalt and pitch: Because of its suspected carcinogenicity, use of pitch as a paving material was prohibited in the USSR in 1950 (Gorbov and Fomenko, 1962). Usage patterns in other nations appear to be economically motivated. No regulations limiting use of asphalt were found.

4. Department of Labor, Occupational Safety and Health Administration (OSHA)

a. Coal Tar Pitch Volatile Standard

Table Z-1 of 29 CFR 1910.1000 specifies that the eight-hour time-weighted average for exposure to "coal tar pitch volatiles (benzene soluble fraction--anthracene, BaP, phenanthrene, acridine, chrysene, pyrene)" shall not exceed 0.2 mg/m^3. This standard does not apply to coke oven emissions.

TABLE VII-1. SOME RECOGNIZED OCCUPATIONAL CANCERS FOR WHICH COMPENSATION IS GIVEN IN VARIOUS COUNTRIES

	PAH	BENZENE	AROMATIC AMINES*
	Skin	hematopoietic System	Bladder
Country			
Australia	+		
Belgium	+		
Federal Republic of Germany	+	+	+**
France	+	+	+
German Democratic Republic			+**
Ireland	+		
Italy	+	+	+
Japan	+		
Switzerland	+		
United Kingdom	+		+**

*α- and β-naphthylamine, benzidine, 4-aminodiphenyl

** Includes cancer of the urinary tract

Source: Montesano and Tomatis, 1977

The interpretation of the coal tar pitch volatile (CTPV) standard (29 CFR 1910.1002) reads as follows:

> "..coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum, wood or other organic matter." (U.S. Department of Labor, 1972, 1977)

The justification for including volatiles from distillation residues of coal, petroleum, etc. is given as follows:

> "Since all of these volatiles have the same basic chemical composition and since all of them present the same basic dangers to a person's health, the standard prescribed by [1910.1000] is applied to the use of all of them." (U.S. Department of Labor, 1972)

Coke oven emissions: 29 CFR 1910.1029 sets the permissible exposure limit at 0.15 mg/m^3 for coke oven emissions, defined as the benzene soluble fraction of total particulate matter (BSFTPM) present during the destructive distillation or carbonization of coal. The Occupational Safety and Health Administration considers the BSFTPM to be the same substance as the benzene soluble fraction of coal tar pitch volatiles, at least those volatiles resulting from coke production (U.S. Department of Labor, 1976). The proposed and final standards for exposure to coke oven emissions discuss alternative approaches to standards designed to regulate complex mixtures of particulates, vapors and gases (U.S. Department of Labor, 1975, 1976). For this reason, the information compiled for the coke oven standards should be reviewed before the final technical standard for coal tar pitch volatiles is promulgated.

b. Coal Tar Pitch Volatile Standard Contested

On at least two occasions, OSHA has attempted to apply the CTPV standard to asphalt fumes, in accordance with 29 CFR 1910.1002 - "Coal tar pitch volatiles: interpretation of term."

Samples of asphalt emissions at two roofing manufacturing companies had benzene soluble fractions in excess of 0.2 mg/m^3, as well as detectable amounts of BaP. The benzene soluble fractions ranged from 0.4 mg/m^3 to 5.4 mg/m^3; the BaP concentrations ranged from 0.06 μg/m^3 to 0.6 μg/m^3. Citations by OSHA were successfully contested before the Occupational Safety and Health Review Commission (OSHRC) by the Celotex Corporation, Cincinnati, Ohio (OSHRC Docket No. 15030)[1] and Bird and Son, Inc., Perth Amboy, New Jersey (OSHRC Docket No. 15553)[2]. Thus there is currently no legal limit on asphalt fume exposure in the workplace.

5. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health (NIOSH)

a. Criteria Document : Asphalt

NIOSH has prepared a criteria document on asphalt fumes, recommending that the level to which any worker can be exposed should not exceed five milligrams total airborne particulates per cubic meter of air, determined during any fifteen minute period. (U.S. National Institute for Occupational Safety and Health, 1977a).

b. Criteria Document: Coal Tar Products

NIOSH has concluded that coal tar, coal tar pitch, creosote and any mixture of these represent a carcinogenic hazard and has recommended that the permissible exposure limit be the lowest concentration that can be reliably detected by current methods. Thus, no worker should be exposed to any of the coal tar products listed above, or mixture of these, in excess of 0.1 milligram of the cyclohexane extractable fraction per cubic meter of air, determined as a time-weighted average for up to a ten hour shift in a forty hour work week (U.S. National Institute for Occupational Safety and Health, 1977b).

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[1] Personal Communication, Janie Brown, U.S. National Institute for Occupational Safety and Health, Cincinnati, Ohio.

[2] Personal Communication, Richard Niemeier, U.S. National Institute for Occupational Safety and Health, Cincinnati, Ohio.

c. Registry of Toxic Effects of Chemical Substances

The Registry of Toxic Effects of Chemical Substances (formerly the Toxic Substances List) is prepared by NIOSH in compliance with requirements of Section 20 (a) (6) of the Occupational Safety and Health Act of 1970, Public Law 91-596. There are entries for "asphalt" and "asphalt (cut back)," but none for "coal tar pitch" or "pitch." The entry for "coal tar, aerosol" refers to the benzene soluble fraction and includes the OSHA standard of 0.2 mg/m^3, although the term CTPV is not mentioned (U.S. National Institute of Occupational Safety and Health, 1976).

B. Consensus and Similiar Standards

1. National Safety Council (NSC)

The NSC considers asphalt a "substantially nontoxic" substance capable of causing dermatitis in certain individuals. It recommends that protective equipment (gloves, goggles) be worn and "personal cleanliness" be practiced by individuals working with asphalt. Skin contact with asphalt and its fumes should be avoided. The solvent vapor concentration of cutback asphalts should be kept below the threshold limit value (National Safety Council, 1965).

For pitch and tar, NSC states that although these materials are known to be producers of skin cancer, high incidences of skin cancer related to exposure have not been reported, in spite of extensive investigations (National Safety Council, 1974). No recommendations for use are given.

2. American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit values of 5 mg/m^3 for asphalt (petroleum) fumes and 0.2 mg/m^3 for coal tar pitch volatiles (benzene soluble fraction) have been established by ACGIH (1971). These values are not legally binding.

VIII. TECHNICAL SUMMARY

Asphalt and coal tar pitch are widely used, durable, cementitious, thermoplastic, water-resistant, bituminous materials. To enhance their durability and versatility, both are used with a variety of materials, including gilsonite, asbestos, epoxy resins, rubber, polyvinyl chloride, mineral aggregates, petroleum coke, coal, creosote, and carbon black. Although technological applications have changed, the basic uses of asphalt and pitch as binders, saturants, and weatherproof coatings have persisted for centuries.

Because asphalt and pitch differ markedly in many important respects, they must be discussed and evaluated as two distinct potential environmental contaminants.

Asphalt

Petroleum asphalt is the uncracked residue from the fractional distillation of crude oil. Natural deposits of asphaltic materials, occurring world-wide, make up one to five percent of all asphalt consumed in the United States. Gilsonite is the most commonly used native asphalt.

Commercial grades of asphalt are prepared to meet standard specifications based on several physical properties, including softening point and viscosity. Base stocks of asphalt can be formulated from an uncracked distillation residue (straight-run asphalt), a residue of propane or butane deasphalting, or an air blown asphalt (a stock through which air is forced at a temperature from 200 to 280°C). Liquid (cutback) asphalts are prepared by diluting base stocks with solvents such as gasoline, naphtha, kerosine, or heavy diesel fuel. Emulsions of asphalt and water are versatile, require less equipment for use than cutbacks, and eliminate exposure to petroleum solvents.

Since 1970 annual asphalt sales in the United States have averaged 31 million tons. Seventy-eight percent of the asphalt is used in paving, 17% in roofing, and 5% in miscellaneous applications (including dam linings, soil stabilizers and electrical insulation).

Although plants manufacturing paving and roofing materials have generally been considered a nuisance because of odor and dense haze, their emissions have not been well characterized. Emissions from such plants and from asphalt air blowing processes include entrained asphalt droplets, carbon dioxide, carbon monoxide, sulfur oxides, nitrogen oxides, aldehydes, hydrogen sulfide, traces of vanadium, nickel, cadmium and lead, as well as a variety of hydrocarbons. The large quantities of particulates emitted may contain up to 0.002% polynuclear aromatic hydrocarbons (PAH), including several carcinogens.

Ninety-nine percent control of the emissions is possible using currently available thermal afterburners (fume incinerators) that retain the effluent gas for 0.5 seconds at more than 816°C. The exhaust gas from the afterburner can pass first through an oil-water gravity separator and then to a wet scrubbing unit. The oil can be recovered from the gravity separator.

Water pollutants from the manufacture of asphalt materials have received little attention. Water from scrubbing units used as the sole emission control device at hot-mix plants can contain clay and mineral particles, sulfuric acid, oil, gasoline, and asphalt.

Installation of paving and roofing materials may be a localized source of air pollution. Emissions from roofing operations can be greatly reduced by maintaining the asphalt kettle temperature evenly below 216°C. Evaporation of low-boiling hydrocarbon solvents from cutback asphalts contributes as much as four percent of atmospheric hydrocarbon pollution in the U.S. Such emissions can be entirely eliminated by the use of aqueous emulsions.

There are 1.7 million miles of asphalt covered roads in the United States. It has been estimated that there are six billion tons of asphalt covering roads, parking lots, runways and playgrounds. These surfaces are subject to biological, chemical and physical degradation. Bituminous (asphalt and pitch) highways may be a minor source of polycyclic aromatic, heterocyclic, and metallic substances, possibly toxic or carcinogenic, in air, waterways and sediments.

Limited animal skin painting and inhalation studies suggest that asphalt may be weakly carcinogenic. No studies on its mutagenic or teratogenic potential have been reported. Studies of exposure of plants, fish or other organisms to asphalt are inadequate but have indicated no harmful effects. Some microorganisms are capable of degrading asphalt.

Few human exposure studies are available. Mixed exposures to asphalt and the more biologically potent coal tar pitch have been common in paving, roofing and weatherproofing operations. It is therefore difficult to determine whether workers are at risk from the asphalt. A few incidents of contact dermatitis and respiratory irritation may have occurred; however, it is generally agreed that asphalt is a relatively safe material to workers under proper working conditions.

The Environmental Protection Agency specifies that new asphalt hot-mix plants must limit particulate emissions to less than 90 mg per dry standard cubic meter and less than 20% opacity. Effluent guidelines for new and existing paving and roofing point sources (using tars and asphalts) regulate levels of oil, grease and total suspended solids. The recommended standard for occupational exposure to asphalt fumes is 5 mg airborne particulates/m^3 (U.S. National Institute for Occupational Health, 1977a). Although the Occupational Safety and Health Administration standard on "coal tar pitch volatiles" has been interpreted to include asphalt, the standard has not been successfully enforced.

Coal Tar Pitch

Crude coal tar is a highly cracked product evolved during carbonization of coal. All coal tar pitch commercially available in the U.S. is the residue of distillation of by-product coke oven tar.

The amount of pitch produced annually has declined from 2,004,000 tons in 1965 to 1,227,000 tons in 1976. About 62% of the pitch is used as a binder or impregnant in carbon and graphite products. The largest single carbon product market is for carbon anodes used in primary aluminum manufacture. About 17% of the pitch produced is burned as an open-hearth furnace fuel. Pitch (7%) is used for the manufacture of "tar" saturated roofing felt, as well as cements used in the built-up roofing process on large, relatively low slope commercial roofs. A stable market for pitch (10,000 tons annually) has been its use as a binder in "clay pigeons" for skeet shooting. Pitch bonded and pitch impregnated refractory brick used to line basic oxygen furnaces, blast furnaces and foundry cupolas represent a steadily growing market.

Pitch can undergo the same basic processing as does asphalt, namely air blowing, dilution with coal tar solvents, or emulsification with water. Air pollution control measures used for asphalt fumes can also be used to contain emissions from pitch. Emissions from manufacturing processes using pitch have not been thoroughly investigated. Large amounts of pitch dust may be present as well as pitch volatiles. Large amounts of volatiles are emitted during prebaking and graphitizing of pitch-containing carbon products such as electrodes. Emissions during use are higher for self-burning (Soderberg) electrodes than for those that have been prebaked or graphitized before use. Pitch fumes usually contain, in addition to many other compounds, carbazole, phenanthrene, anthracene, acridine, pyrene, and benzo(a) pyrene. Pitch volatiles or coal tar volatiles can contain zinc, lead, vanadium, cadmium, nickel, copper and chromium.

Workers exposed to pitch and sunlight often develop moderate to severe acute phototoxic reactions of the skin. Effects of prolonged exposure to pitch and sunlight have not been studied. Chronic exposure of the eyes to pitch may lead to permanent changes.

Studies of human populations exposed to pitch and coal tar confirm that these materials are skin carcinogens (U.S. National Institute for Occupational Safety and Health, 1977b). Because fumes and particulates are inhaled during exposure, increased incidence of lung cancer has been suspected, although highly significant elevations have not been found in the limited epidemiological studies reported. In workers exposed to pitch but not to other fractions of coal tar, there may be an increased risk of mortality from cancer of the buccal cavity, larynx, pharynx, esophagus, stomach, and possibly bladder. In complex exposures such as coke ovens, gas works, and tar distilleries, the contribution of pitch to the observed increased cancer risk is uncertain. Even in less complex exposures, the importance of multiple factors in cancer production makes it difficult to evaluate the contribution of coal tar pitch to carcinogenic potency.

Although coal tar is generally known to contain carcinogenic PAH such as BaP and to produce skin cancer in experimental animals, medications based on crude coal tar have been widely used for the prolonged treatment of chronic skin diseases such as psoriasis and eczema. Few, if any, cases of human cancer following such use have been documented, and few studies have been performed in experimental animals. The limited evidence available indicates that such medications do contain carcinogenic PAH including BaP and do cause cancer in treated animals.

Some components of pitch fumes are toxic to vegetation in the presence of sunlight. The use of pitch to waterproof timber and water pipes may result in the gradual solubilization of potentially carcinogenic polynuclear aromatic hydrocarbons or other toxic substances.

Some attempt has been made to control worker exposure to emissions from coal tar pitch. The present "coal tar pitch volatile" standard (U.S. Department of Labor, 1977) specifies that worker exposure to airborne concentrations of pitch volatiles (benzene soluble fraction) shall not exceed 0.2 mg/m^3 averaged over an eight-hour work shift. The final technical standard, when promulgated by the Department of Labor, will delineate requirements for worker education, medical surveillance, personal hygiene measures, and protective equipment (including respirators) as well as accident, spill, fire and disposal procedures for any substance defined under the standard. The current interpretation of the coal tar pitch volatile standard covers volatiles from distillation residues not only of coal, but also of other organic materials including petroleum (i.e., asphalt). Because coal tar pitch volatiles are considered carcinogenic the National Institute for Occupational Safety and Health (1977b) has recommended a standard for occupational exposure to coal tar products, including coal tar pitch, of 0.1 mg cyclohexane solubles per cubic meter of air (the lowest detectable limits).

Examination of the literature indicates that the biological effects of asphalt are probably limited. Large quantities, however, are processed and the major uses are in roofing and paving products that are permanently exposed to slow degradation in the environment. Coal tar pitch, on the other hand, produces acute effects in a large proportion of exposed workers as well as an increased risk of cancer of several sites after prolonged exposure. The major uses of pitch involve occupational exposure, where workers can be protected and emissions can be controlled, rather than environmental exposure.

IX. CONCLUSIONS AND RECOMMENDATIONS

Although asphalt and coal tar pitch are similar in certain physical properties characteristic of bitumens, examination of the literature indicates that they differ markedly in origin, composition, major uses, and severity of biological effects. Therefore the two materials should be handled separately in risk evaluation and in regulation of occupational exposure and of emissions to the environment.

Although asphalt appears to be less harmful to humans and animals than is coal tar pitch, the major uses of asphalt are in large surfaces permanently exposed to weathering processes. The acute and prolonged effects of coal tar pitch are more severe and may affect a large proportion of exposed workers. If industrial emissions from pitch are controlled and use of pitch in exposed surfaces is severely restricted, however, the overall contribution of coal tar pitch to environmental pollution may be less than that of asphalt.

This report is limited to consideration of petroleum asphalt and coal tar pitch. However, certain related materials may present similar hazards and should be evaluated separately. Such materials include the distillate fractions from crude coal tar and also the tarry residues produced from other fossil fuel conversion processes.

There is reason to believe that the high boiling distillate fractions of coal tar, such as creosote oil and anthracene oil, contain significant amounts of carcinogenic PAH and have caused human and experimental cancers when used, for instance, as lubricant oils in the metal-working industry.

As petroleum and asphalt supplies become insufficient for present and future requirements, coal and oil shale conversion processes will probably increase, producing large quantities of tarry residues. Disposal of these materials may present a significant problem. It will be tempting to use such tars to replace asphalt as bitumens for paving and roofing, which would result in large-scale exposure and environmental pollution. These tars resulting from high temperature pyrolysis can be expected to be at least as hazardous as coal tars obtained from present coking operations. Therefore it is important that investigations should be conducted early enough to ensure proper design of equipment and adequate protection of workers, the public, and the environment.

Evaluation of the environmental and occupational hazards of asphalts and tars is complicated by major inconsistencies in the terminology used by producers, purchasers, users, epidemiologists, physicians, and experimental scientists. "Asphalt," as used here, refers to native asphalt or to the distillation residue (petroleum asphalt), essentially uncracked, from straight-run processing of petroleum. This product is distinguished from severely cracked petroleum residues such as petroleum pitch. "Coal tar pitch" is here defined as the residual product remaining after distillation or stripping of crude coal tar (a cracked material) formed during the coking of coal. Both the origin and the composition of "asphalt" are thus distinct from those of "pitch."

For the purpose of this report, terms such as tar, coal tar, coal tar pitch volatiles, and PPOM (polycyclic particulate organic matter) are used with caution. Clear and consistent definitions of terms for general use are needed. Published reports of all original studies should include specific descriptions of the materials investigated so that comparisons with other studies can be made.

Although a number of methods for sampling, analysis, and monitoring of bituminous materials have been developed, few are well standardized or suited for routine use. In particular, sampling devices should be improved, with special attention to development of filters or other samplers that collect all of the chemical substances and particle sizes under investigation. Procedures for the determination of a greater number of individual PAH should be standardized so that a variety of potentially hazardous materials can be monitored instead of only BaP. Because of the health hazard of benzene, a safer solvent should be selected for use in standard analytical procedures.

Although effective devices exist for the control of emissions from the production and processing of asphalt and pitch and for some uses, they are not always utilized. More data are needed on the actual levels of pollutants now being emitted. There is a need for more energy-effective control devices and for control of emissions during exposed uses such as roofing. Incentives for adequate control of harmful emission are also needed.

Although methods do exist for sampling and analysis of total particulates, benzene solubles, and individual polynuclear aromatic compounds, no satisfactory relationship has been established between the levels of the measured materials and the degree of hazard from exposure to the asphalt or coal tar pitch sampled.

A few experimental studies have investigated the composition and biological effects of asphalts and of coal tars. Such studies have indicated the relatively low hazard of asphalt and the significant phototoxicity and carcinogenicity of coal tar pitches. Although the effects of the two groups of materials are different, their physical properties are so similar that their uses overlap. Thus it is difficult to find human exposures to asphalt without simultaneous exposure to mixtures containing bituminous materials derived from coal tar or from petroleum cracking operations, either of which are more hazardous than asphalt. The problem of identifying asphalt as an entity distinct from coal tar has been investigated by the U.S. National Institute for Occupational Safety and Health (1977a) for the case of asphalt fumes. However, the only way that workers or the public can profit from this distinction is by limiting or excluding the use of coal tar in combination with asphalt, and at the same time finding safe uses for the coal tar pitch.

The most serious hazard to human health from these bituminous materials appears to be the carcinogenic potential of PAH present in the materials or in the work environment during processing, application, and end use. While the nature of the carcinogens is similar in asphalt and in pitch, the concentrations are much greater in coal tar pitch and other cracked residues than in the relatively uncracked asphalt. Studies of correlation of biological effects with chemical composition and processing history of specific samples would provide helpful information.

Measurable indexes of pollution such as benzene solubles, total particulates, or respirable particulates which have been used or considered as standards for limitation of exposure are associated with widely different levels of PAH in asphalt and in pitch. The proportion of carcinogen in the total PAH may also differ. The possible cocarcinogenic effects of other components of asphalt and pitch may also vary widely. Little information is available about these multiple factors and their possible relationship in asphalt and in pitch. Until such information has been obtained and verified in well designed experiments, valid standards for safe levels of exposure cannot be established.

To permit comparison and evaluation of experimental studies, the nature of the material being tested should be specified clearly. Where possible, exposure to asphalt and to pitch should be studied separately. Routes of exposure should be similar to those found in humans. Inhalation studies are particularly needed. Skin exposures to samples in various physical states should be conducted to determine whether, as has been claimed, pitch dust is more hazardous than liquid or pelleted forms. Samples of benzene solubles, total particulates, or other materials which may be considered as the basis of standards should be tested to determine whether their biological effects actually correspond to their assigned level of hazard. In addition to being tested for carcinogenicity, these complex materials should also be tested as possible cocarcinogens or inhibitors of carcinogenesis. Because asphalt and pitch are often used in combination with other materials such as mineral aggregates, solvents, and other bitumens, the effects of such materials on the biological properties of asphalt and pitch should be studied. The role of multiple factors in the carcinogenicity of asphalt and pitch needs continued emphasis.

Although less serious than carcinogenicity, phototoxicity is observed in a large proportion of workers exposed to coal tar pitch. Studies are needed to determine the causative agents in pitch, methods of protecting workers, and possible chronic effects of repeated episodes of photosensitization.

Epidemiological studies are needed for industrial workers (pavers, roofers, aluminum and other metallurgical workers) and for users of coal tar medications. However, epidemiological studies of asphalt and coal tar pitch exposures may be of limited value in identifying a causative agent because of the uncertain and often mixed nature of the exposure. Since coal tar pitch appears to be more carcinogenic than asphalt, any exposure that includes coal tar pitch (such as roofing) can offer little information about the possible carcinogenic hazard of asphalt.

The initial need in epidemiological studies is the preparation of careful job descriptions which can be correlated with route and degree of exposure to specific materials. Such information is needed for roofing and paving jobs, where exposure may be severe and accompanied by exposure to sunlight, and hygienic facilities may be limited. This information may be particularly difficult to obtain because records of job histories and materials handled are inadequate.

The trace metal content has been studied extensively for petroleum, for coal from various geographical sources, and for the emissions from combustion of these fossil fuels. Little has been reported about the metal content of coal tars to indicate whether any potentially toxic trace metals are being concentrated in the tarry residue. More work is needed to determine whether trace metals constitute a hazard in asphalts and tars, or whether such metals will be leached appreciably under conditions of exposure during use of bitumens.

Present regulations by the Environmental Protection Agency limit particulate emissions from asphalt concrete plants and effluents from paving and roofing material point sources. Because even small amounts of carcinogenic polynuclear aromatic compounds contribute to the total carcinogenic burden to which the public is exposed, emissions from both asphalt and coal tar pitch operations should be monitored and controlled.

Because of the immediate and long-term effects on the health of exposed workers, there is a need for limitation of occupational exposure to coal tar pitch and possibly to asphalt. U.S. Department of Labor limitations of occupational exposure because of possible carcinogenic hazard are based on a definition of "coal tar pitch volatiles" which considers the benzene soluble fractions volatilizing from distillation residues of any organic materials, including petroleum as well as coal, as having the same basic chemical composition and presenting the same dangers to human health. Because the chemical composition of asphalt differs widely from that of coal tar pitch, both quantitatively and qualitatively, the present standard for coal tar pitch volatiles, with its definition including asphalt, cannot be applied successfully to both materials. Separate standards are needed for the control of exposure to and emissions from asphalt and coal tar pitch.

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